

THE
LONDON, EDINBURGH, AND DUBLIN
PHILOSOPHICAL MAGAZINE
AND
JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

NOVEMBER 1926.

LXXX. *The Theory of the Vane Anemometer.* By E. OWER,
A.C.G.I., B.Sc. (*National Physical Laboratory*)*.

1.1. **A**LTHOUGH the vane anemometer has been in fairly common use for a considerable time, its behaviour has not hitherto been subjected to theoretical treatment, and consequently does not appear to be completely understood. As a means of measuring wind speed, more particularly, perhaps, in the range of low speeds where such small pressures are set up by the motion that their accurate determination becomes a matter of considerable difficulty, its simplicity renders it an exceedingly useful instrument, and if properly used it is capable of giving all the precision ordinarily required.

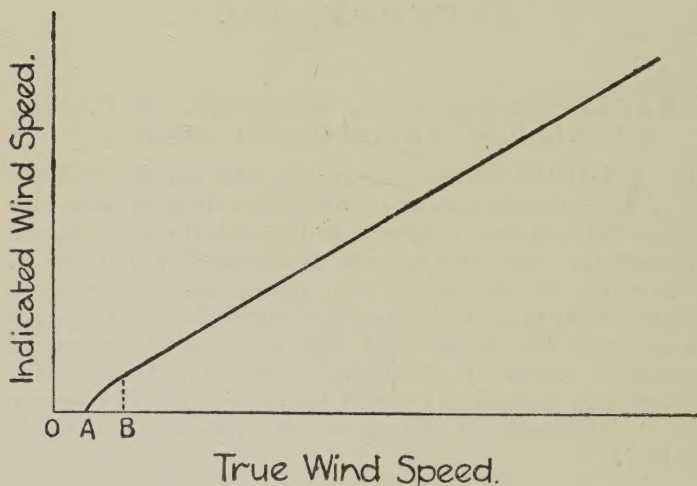
1.2. Before proceeding to a detailed analysis, we shall find it useful, in order to define the problem for consideration, to examine briefly the construction of the instrument. It consists, as is well known, of a number of flat light vanes, mounted on radial arms rigidly attached to a common spindle. The latter is placed along the wind direction and the vanes are inclined to the wind in such a manner that a torque is produced which causes them to rotate in a path perpendicular to the wind direction and at a speed which is a definite function of the wind speed. The motion of the spindle is communicated by suitable gearing to a pointer moving over a graduated dial. Normally, the dial is graduated in feet,

* Communicated by Mr. R. V. Southwell, F.R.S.

and experience has taught manufacturers of these instruments how to proportion the various dimensions, vane inclinations, and gearing ratios so that the number of feet indicated on the dial in unit time is more or less equal to the distance traversed by the wind in the same time, *i. e.*, to the wind speed.

1.3. It will be apparent from the foregoing remarks that the speed of rotation of a given set of vanes will be determined not only by the wind speed, but also by the mechanical friction introduced at the spindle bearings and by the gearing. In the ideal case where friction is entirely absent, the curve of indicated wind speed against true wind speed will be a

Fig. 1.



straight line passing through the origin (this is shown below, equation (2)) whose slope will be determined by the inclination of the vanes to the wind direction. In practice, however, friction has an appreciable effect, especially at low speeds when the wind forces on the vanes are small, and the usual calibration curve of a vane anemometer is as shown in fig. 1. At high speeds the curve in nearly every case exhibits no sensible departure from linearity, but at low speeds it bends over somewhat in the manner shown, the abscissa *OA* representing the true wind speed at which the vanes just commence to turn. The values of the wind speed corresponding to *OA* and to *OB* (above which the curve is linear) vary, as is to be expected, with different instruments; in a very sensitive anemometer specially designed for use at low speeds *OA* was

found to be about 0.5 feet per second, and OB about 1.0 feet per second.

1.4. This brief exposition of the characteristics of these instruments serves to define the limitations to which they are subject. It is often stated that vane anemometers are unreliable and give inconsistent readings which cannot be explained. The writer has, however, had considerable experience with the instruments, which certainly does not bear out these remarks. It appears probable that trouble frequently arises through the use of an instrument to measure wind speeds for which it is not suitable. It is not ordinarily advisable, for example, to attempt to measure speeds less than OB, which fall on the lower curved part of the calibration curve. On the other hand, if the speed is too high the vanes may suffer a permanent angular distortion which will cause a corresponding permanent alteration in the calibration curve. Most makers supply an instrument for general use which may safely be used for speeds ranging from 5 or 10 to 50 feet per second. For speeds higher than this special instruments of heavier construction can be obtained; for lower speeds instruments of the form designed by the writer* may be used with advantage, and will be found to give consistent readings down to about 0.6 feet per second.

1.5. A further point which must be remembered is that every instrument must be calibrated in a wind tunnel or on a whirling arm where the wind speed relative to the vanes can be regulated and measured by independent means. It is exceptional for two instruments made to the identical pattern and dimensions to have identical calibration curves.

2.1. In a theoretical discussion of the vane anemometer we have to consider a number of conditions. The relation between indicated and true speed shown by the curve of fig. 1 holds only for the case in which the instrument is placed in a steady wind, whose speed is uniform across the whole vane circle. In practice, however, these conditions are not usually realized, and we have the following three cases to consider:—

- (a) Readings obtained in a fluctuating wind.
- (b) Effect of variation of air density.
- (c) Readings obtained when the wind speed varies across the vane circle.

* A description of this instrument appeared in the 'Journal of Scientific Instruments,' vol. iii., January 1926, p. 109.

2.2.

EQUATIONS OF MOTION.

Notation.

F = air force on blade.

T = frictional torque.

Q = wind torque.

V = wind velocity.

 v = linear tangential velocity of centre of pressure of blades. $\bar{V} = \sqrt{V^2 + v^2}$ = velocity of wind relative to blade. n = rotational speed of blades.

A = area of one blade.

D = outside diameter of blade circle.

 m = number of blades. r = distance of centre of pressure of blade from axis of rotation. ρ = air density = $\frac{\text{weight per unit volume}}{g}$.

N = rotational speed of pointer.

C = gearing constant, such that $N = Cv$.

K = wind force coefficient (see below).

 θ = inclination of blade to wind direction. ϕ = inclination of blade to relative wind (= "incidence" of blade). γ = angle of resultant wind force on blade to relative wind direction.

I = total amount of inertia of all blades about axis of rotation.

 g = acceleration due to gravity.(i.) *Fundamental Equation.*

The anemometer may be regarded as a windmill, and aerodynamic theory has established the fact that for a windmill the wind torque Q may be written

$$\frac{Q}{\rho V^2 D^3} = f\left(\frac{nD}{V}\right), \quad (1)$$

where $f(nD/V)$ represents some function of (nD/V) which has to be determined.

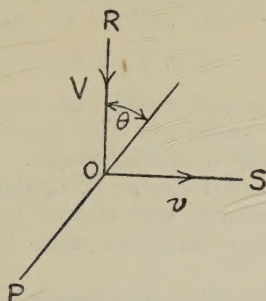
(ii.) *Equations for Particular Cases.*

(a) *Mechanical Friction Absent.*

Let PQ (fig. 2) represent one blade inclined at an angle θ to the wind, and let O be the centre of pressure of the blade. (It should be noted that the blade is rotating in a circular path perpendicular to the plane of the paper.) The blade PQ will move instantaneously along OS, perpendicular to the wind direction RO, with a velocity v such that the resultant of V and v lies along QP,

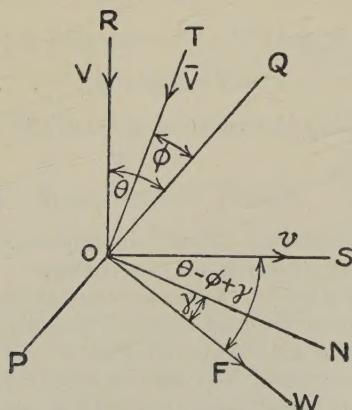
$$\begin{aligned} \text{i. e.} \quad & v = V \tan \theta, \\ \text{and} \quad & N = Cv = CV \tan \theta. \quad \dots \quad (2) \end{aligned}$$

Fig. 2.



In this case, therefore, the calibration curve of the instrument will be a straight line passing through the origin.

Fig. 3.



(b) *Mechanical Friction Present.*

The velocity diagram now becomes more complicated, and it is necessary to consider the forces acting on the blade.

PQ will still move along OS perpendicular to the wind direction but at a lower speed v so that the resultant of V and v , i. e., the wind speed \bar{V} relative to the blade, will now be inclined at an angle ϕ to the plane of the blade. The blade now becomes a flat plate inclined to the wind at an angle of incidence ϕ , and there will be a resultant force F on the blade acting along OW inclined at an angle γ to ON the normal to the relative wind direction. The component of F along OS multiplied by the distance of O from the centre of rotation and by the number of blades, supplies the torque which overcomes the resisting torque due to mechanical friction.

Now from experiments on the forces acting on flat plates in moving currents of air we have the equation

$$F = K\rho V^2 A\alpha,$$

where K is a numerical coefficient depending on the incidence α of the plate, and the other symbols have the significance tabulated in the list above.

Neglecting the inflow factor (*i. e.*, slowing up of the air entering the vane circle) and mutual interference between the blades*, we may therefore write for the blade under consideration

$$F = K\rho \bar{V}^2 A\phi.$$

Resolving along OS, putting $\bar{V}^2 = V^2 + v^2$, and equating the wind torque to the frictional torque, we therefore have for steady motion

$$T = K\rho\phi A(V^2 + v^2)mr \cos(\theta - \phi + \gamma). \quad (3)$$

Also $v = V \tan(\theta - \phi), \quad (4)$

so that, substituting the value of ϕ from (3) in (4), we have

$$v = V \tan \left[\theta - \frac{T}{K\rho A(V^2 + v^2)mr \cos(\theta - \phi + \gamma)} \right]. \quad (5)$$

The utility of equation (5) will be apparent later when we consider the effect of variation of density.

From consideration of (4) we see that at high speeds when the relative effect of friction is small in comparison with the wind forces, ϕ is small compared with θ and the calibration curve of the instrument will be practically linear. At low speeds ϕ becomes large compared with θ , and v will be zero at a certain low value of V when ϕ becomes equal to θ .

* The construction of the instrument and the conditions under which it works are such as to warrant the assumption that both these effects will be small.

2.3. CALCULATION OF THE MECHANICAL FRICTION TORQUE T .

A knowledge of T is required for the solution of the first and third of the problems stated above (see 2.1). Obviously, the mechanical friction will depend upon the construction of the anemometer so that it cannot be computed from first principles; it has to be determined separately for every instrument by experiment. The necessary tests, however, are simple and comprise only a calibration to establish the relation between v and V for a number of values of the wind speed V . By the use of equations (3) and (4) T can then be calculated for different values of V , as follows.

Fig. 4.

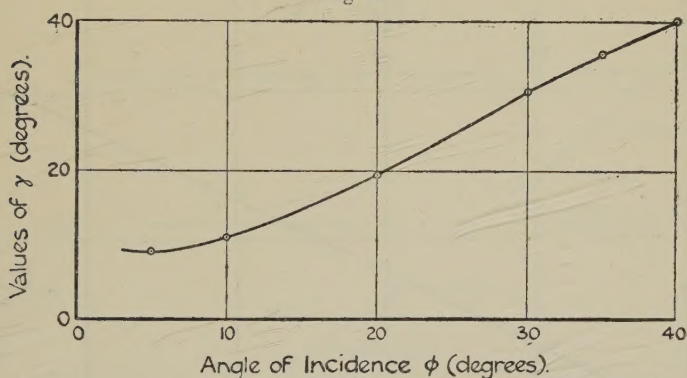
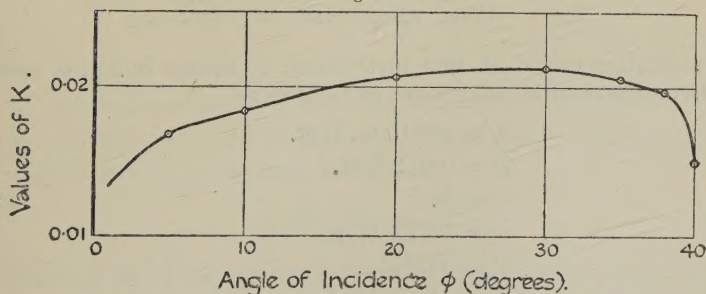


Fig. 5.



For a given V , the value of v is known from the calibration curve, so that ϕ can be determined from equation (4), θ being a measurable dimension in the instrument. The angle ϕ now represents the effective incidence of the blade for the conditions under consideration, and K and γ can therefore be determined from the aerodynamic characteristics of flat plates found experimentally by G. Eiffel*. For convenience, these quantities are reproduced, for the case of square plates,

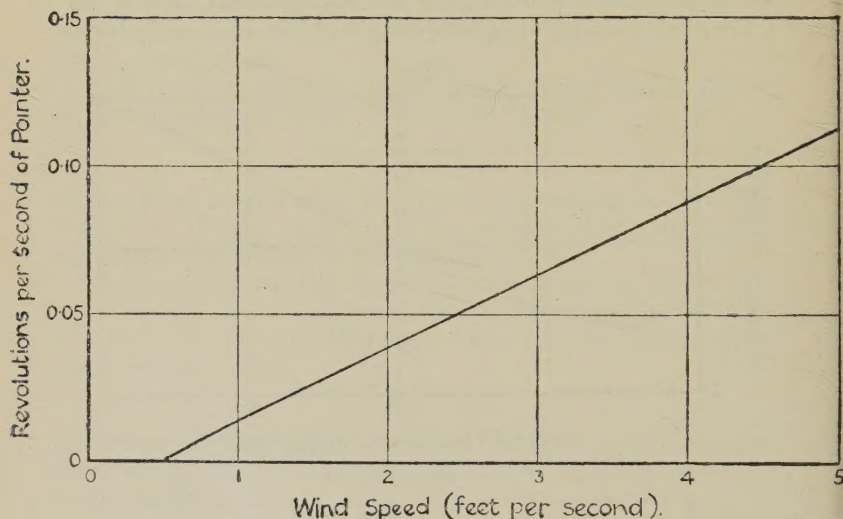
* 'La Résistance de l'Air et l'Aviation,' p. 134.

in figs. 4 and 5. (It is sufficiently close for our purpose to take square plate characteristics.) All the quantities in equation (4) are now known with the exception of T , which can therefore be calculated.

Calculations of T have been made in this manner for the writer's low speed vane anemometer mentioned above*. The

Fig. 6.

Calibration Curve for Low-Speed Anemometer.



calibration curve of this instrument is shown in fig. 6, and its mechanical constants are as follows:—

$$A = 0.007 \text{ sq. feet.}$$

$$D = 0.312 \text{ feet.}$$

$$m = 8.$$

$$r = 0.125 \text{ feet.}$$

$$C = 0.0254.$$

$$I = 192 \times 10^{-8} \text{ slugs ft.}^2$$

$$\text{ratio} \frac{\text{revs. of pointer}}{\text{revs. of vanes}} = \frac{1}{50}.$$

For steady motion $Q = -T$, and the values of T obtained in the manner just indicated were inserted in equation (1),

and a curve of $\frac{Q}{\rho V^2 D^3}$ against $\frac{nD}{V}$ was plotted. This curve

* *Loc. cit.*

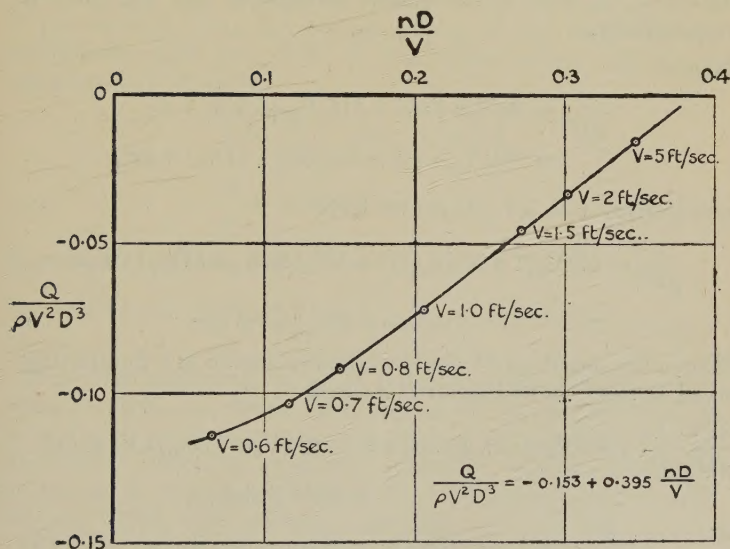
is reproduced in fig. 7 ; it will be seen that above $V = 1$ foot per second the curve is linear and can be expressed in the form

$$\frac{Q}{\rho V^2 D^3} = -0.153 + 0.395 \frac{nD}{V}, \quad \dots \quad (6)$$

so that, incidentally,

$$f\left(\frac{nD}{V}\right) = -0.153 + 0.395 \frac{nD}{V}.$$

Fig. 7.



It appears, therefore, that over the linear part of the calibration curve we may write

$$\frac{Q}{\rho V^2 D^3} = a + b \frac{nD}{V}, \quad \dots \quad (7)$$

where a and b are constants, and this result may be expected to apply, in the region of linearity, to all instruments, the values of a and b varying from one to another.

3.1. EFFECT OF A FLUCTUATING AIR SPEED.

In order to investigate analytically the effect of a fluctuating wind speed, we may assume that V at any time t is given by the simple harmonic relation

$$V = V_0(1 + \lambda \sin pt), \quad \dots \quad (8)$$

where V_0 is the value of V at time t_0 .

We will imagine this fluctuating speed suddenly impressed upon the anemometer which was previously rotating at a steady rate n in a steady wind of speed V_0 .

From equation (7), we have, at time $t = 0$

$$Q_0 = \rho V_0^2 D^3 \left(a + b \frac{n_0 D}{V_0} \right),$$

and at time $t = t$ shortly after

$$Q_1 = Q_0 + q = \rho (V_0 + v)^2 D^3 \left\{ a + b \frac{n_0 + n}{V_0 + v} D \right\},$$

where q , v , and n are small changes in Q_0 , V_0 , and n_0 respectively.

Hence

$$\begin{aligned} \frac{q}{\rho D^3} &= 2aV_0v + av^2 + bD(V_0 + v)(n_0 + n) \\ &= bD(V_0 + v)n + v(2aV_0 + bDn_0) + av^2, \end{aligned}$$

and putting $v = \lambda V_0 \sin pt$, we have

$$\begin{aligned} \frac{q}{\rho D^3} &= bDV_0(1 + \lambda \sin pt)n + \lambda V_0(2aV_0 + bDn_0) \sin pt \\ &\quad + a\lambda^2 V_0^2 \sin^2 pt. \end{aligned}$$

Hence the equation of motion for the rotation in a fluctuating wind of the assumed nature becomes

$$\begin{aligned} \frac{2\pi I}{\rho D^3} \frac{dn}{dt} + bDV_0(1 + \lambda \sin pt)n &= -(2aV_0 + bDn_0)\lambda V_0 \sin pt \\ &\quad - a\lambda^2 V_0^2 \sin^2 pt, \end{aligned}$$

$$\text{or} \quad \frac{dn}{dt} + \alpha(1 + \lambda \sin pt)n = \beta \sin pt + \gamma \sin^2 pt, \quad (9)$$

where

$$\left. \begin{aligned} \alpha &= \frac{bDV_0\rho D^3}{2\pi I}, \\ \beta &= -\frac{\lambda V_0(2aV_0 + bDn_0)\rho D^3}{2\pi I}, \end{aligned} \right\} \dots (9a)$$

and

$$\gamma = -\frac{a\lambda^2 V_0^2 \rho D^3}{2\pi I}.$$

The solution of (9) is

$$ne^{\left(t - \frac{\lambda}{p} \cos pt\right)} = \int (\beta \sin pt + \gamma \sin^2 pt) e^{a\left(t - \frac{\lambda}{p} \cos pt\right)} dt + C_1. \quad (10)$$

This solution cannot be reduced further without making certain assumptions based on practical considerations. We have assumed that the wind speed varies according to a sine law about a mean value V_0 , but have not yet assigned magnitudes to the amplitude or period of the variation. In practice, the frequency of the fluctuations in an artificial air current is of the order of one or two per second, and we may further justifiably suppose that some effort is being made to maintain the speed reasonably constant (we must exclude natural winds from consideration), so that it is unlikely that the speed will vary by more than ± 10 per cent. from the mean. We will therefore assume that the frequency is 2 per second (*i. e.*, the periodic time is $1/2$ sec.) and the amplitude ± 10 per cent. of the mean speed. Hence in equation (8) we have

$$p = \frac{2\pi}{1/2} \quad \text{and} \quad \lambda = 0.1,$$

$$\text{i. e.,} \quad \frac{\lambda}{p} = 0.008.$$

Equation (10) then becomes

$$ne^{\alpha(t-0.008 \cos pt)} = \int (\beta \sin pt + \gamma \sin^2 pt) e^{\alpha(t-0.008 \cos pt)} dt + C_1.$$

Now the maximum value of $0.008 \cos pt$ is 0.008 , so that when $t = 0.8$, *i. e.*, before the motion has proceeded for one second, this term becomes less than 1 per cent. of t , and afterwards becomes relatively smaller. It is therefore legitimate to neglect $0.008 \cos pt$ in comparison with t , and we may write, with sufficient accuracy,

$$ne^{\alpha t} = \int (\beta \sin pt + \gamma \sin^2 pt) e^{\alpha t} dt + C_1,$$

the right-hand side of which can now be integrated, giving, after reduction,

$$n = \frac{\beta(\alpha \sin pt - p \cos pt)}{\alpha^2 + p^2} + \frac{\gamma(\alpha^2 + 4p^2 - \alpha^2 \cos 2pt - 2\alpha p \sin 2pt)}{2\alpha(\alpha^2 + 4p^2)} + C_1 e^{-\alpha t} \quad \dots \quad (11)$$

The value of the constant C_1 can be obtained by putting $n = 0$ when $t = 0$ since n is the change in the rotational speed of the vanes from its value at the commencement of the fluctuating motion. We are, however, not concerned with the value of C_1 since the term $C_1 e^{-\alpha t}$ represents a

quickly damped initial disturbance *. The motion therefore rapidly assumes a steady periodic character represented by the first two terms of (11), and the average value of n can easily be seen to be $\gamma/2\alpha$. Substituting the values of γ and α given above (9a), we obtain finally :—

$$\text{Average value of rotational speed above mean} = -\frac{a\lambda^2}{2bD} V_0,$$

where V_0 represents the mean about which the wind speed fluctuates, and the mean rotational speed will be that taken at speed V_0 from the calibration curve obtained in a steady wind.

In other words, this implies that the anemometer, when placed in a wind fluctuating in the assumed manner about a mean value V_0 , will rotate at an average rate higher by $\gamma/2\alpha$ than the rate at which it would rotate in a steady wind speed V_0 ; *i.e.*, an anemometer in a fluctuating wind gives readings in excess of the mean wind speed.

It will be seen that the quantity $\frac{\gamma}{2\alpha} (= -\frac{a\lambda^2}{2bD} V_0)$ is independent of the period of the fluctuations in the wind speed and of the moment of inertia of the vanes. It appears that these quantities will merely determine the lag of the periodic motion of the vanes behind that of the wind, whilst the mean amplitude of the motion of the vanes is affected only by the amplitude of the variations of the wind speed. (An inspection of (11), however, shows that the *actual* value of n at any time is influenced by p and I ; it is only the *average* value of n that is independent of these quantities.)

To obtain some idea of the magnitude of the excess reading obtained in a fluctuating wind, we may apply this result to the low-speed anemometer to which reference has already been made. The values of a and b are given in equation (6), and the value of D will be found in the list of constants for this instrument. The value of $-\frac{a\lambda^2}{2bD} V_0$ will be found to become $0.0062 V_0$ (a is negative), assuming λ as before to be 0.1. We can now draw up the following table in which the value of $0.0062 V_0$ is shown for various values of V_0 ; the value of n_0 corresponding to each value of V_0 was derived from the calibration curve obtained in a steady wind (see fig. 6), and the last column, in which $0.0062 V_0$ is expressed as a percentage of n_0 , shows the percentage increase in the

* In the case of the author's low-speed anemometer this disturbance is reduced to 1/10 of its initial amplitude in just over 3 seconds when $V_0 = 1$ foot per sec., and in correspondingly shorter times as V_0 increases.

readings of the instrument when placed in the fluctuating wind of mean speed V_0 . If the instrument read the true mean speed, this percentage would be zero; actually it is not zero, but is always less than 1 per cent. As the assumed value of λ is probably on the high side, if we consider only those cases in which measurements are made of the speed of air currents produced by fans running at speeds which are intended to be maintained constant, it appears legitimate to assume that in practice the effect of a fluctuating wind on the readings of an anemometer may usually be neglected.

V_0 Feet per sec.	$0.0062 V_0$ revs. per sec.	n_0 revs. per sec.	Percentage error in reading of anemometer.
1	0.0062	0.660	0.94
2	0.0124	1.93	0.64
3	0.0186	3.15	0.59
4	0.0248	4.31	0.57 ₅
5	0.0310	5.56	0.56

3.2. EFFECT OF VARIATION OF AIR DENSITY.

From equations (3) and (4) it will be seen that the value of ϕ depends partly on the air density ρ , so that the calibration of the anemometer will vary somewhat with ρ . Equation (2), however, which gives the calibration curve when mechanical friction is neglected, shows that in this case ρ does not appear. It seems probable, therefore, that at the higher wind speeds, when frictional forces are relatively small compared with the air forces, the effect of variations in ρ will be small and may be neglected. But if an anemometer is employed for the measurement of low wind speeds, for which purpose it has an eminent superiority over other instruments, it is necessary to investigate more closely the effect of a variation in ρ . Errors may then arise on account of the fact that when measurements are being taken the air density may differ somewhat from that existing at the time when the instrument was calibrated, for which conditions only the calibration curve is strictly valid. The writer has already investigated this effect in a communication

to the 'Journal of Scientific Instruments'*, but for the sake of completeness he has thought it advisable to reproduce it briefly here. He wishes to acknowledge the courtesy of the Editor of that Journal for permitting him to do so.

Equations (3), (4) and (5) are employed for this purpose. Let suffixes 0 refer to the conditions under which the instrument was calibrated, and suffixes 1 to the conditions under which measurements are being made, *i. e.*, when the air density has changed from ρ_0 to ρ_1 . For any given value of V , v_0 can be obtained from the calibration curve, and the frictional torque T_0 and ϕ_0 can be obtained from equations (3) and (4). The new value of ϕ when the density is ρ_1 is given by

$$\phi_1 = \frac{T_1}{K_1 \rho_1 A (V^2 + v_1^2) m r \cos (\theta - \phi_1 + \gamma_1)} \quad (12)$$

Now, in practice the air density does not frequently change by more than about 3 per cent., although extreme variations of over 4 per cent. are occasionally experienced. In any case, the change is always small, so that we can assume that the frictional torque is unchanged, *i. e.*, that $T_1 = T_0$. We therefore have the two equations

$$\phi_1 = \frac{T_0}{K_1 \rho_1 A (V^2 + v_1^2) m r \cos (\theta - \phi_1 + \gamma_1)} \quad (13)$$

and

$$v_1 = V \tan(\theta - \phi_1), \quad (14)$$

which are theoretically sufficient for the determination of ϕ_1 and v_1 if the small variations in γ are neglected.

Actually, however, the solution is complicated, and it is quicker to resort to the following method of successive approximation:—Since we are dealing with small changes, a first approximation to the value of ϕ_1 is obtained by assuming that $v_1 = v_0$, $K_1 = K_0$, and $\gamma_1 = \gamma_0$. Equation (13) then becomes, if the value of T_0 from (3) is inserted,

$$\phi_1 = \frac{\rho_0}{\rho_1} \phi_0.$$

By substituting this value of ϕ_1 in (4) a first approximation to the value of v_1 is obtained. We can now calculate $(V^2 + v_1^2)$ and get first approximations to the values of K_1 and γ_1 , and, by putting these in (13), obtain a second approximation to ϕ_1 and hence to v_1 . The process can be

* *Loc. cit.*

repeated a further stage, if desired, but two approximations will usually be found to be sufficient.

The following table shows the results of calculations made in this manner for the author's low speed anemometer, on the assumption that ρ is 3 per cent. in excess of its value at which the calibration curve was obtained.

Wind speed V. Feet per sec.	Air density.		Percentage change in v $= 100 \times \frac{v_1 - v_0}{v_0}$
	ρ_0	$1.03 \rho_0$	
	Linear blade speed v_0 . Feet per sec.	Linear blade speed v_1 . Feet per sec.	
0.7	0.204	0.219	7.2
0.8	0.303	0.319	5.3
1.0	0.519	0.533	2.7
1.5	1.021	1.032	1.1
2.0	1.520	1.531	0.7
5.0	4.37	4.39	0.5

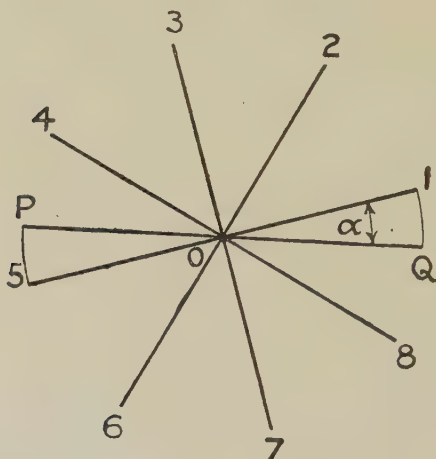
From these results it will be seen that the effect of variations in ρ may be appreciable at low speeds and should be considered for accurate work. Although the assumed change in ρ is somewhat on the high side, it should be pointed out that the instrument to which these results relate was specially designed for low speed work, the construction being carefully carried out with a view to reducing mechanical friction to a minimum. The table emphasizes the danger of using unsuitable instruments for low speed measurements and the desirability of measuring and recording the air density at which the instrument was calibrated and that obtaining during subsequent experiments at low speeds. For high speeds this refinement is unnecessary.

3.3. EFFECT OF A VARIATION IN WIND SPEED ACROSS THE VANE CIRCLE.

In general the distribution of velocity across a pipe along which air is flowing is not uniform, the velocity being higher at the centre than near the walls. It is well known that in order to determine the quantity of air flowing in such

a case, the velocity has to be measured at certain definite radii, which are the mean radii of a number of imaginary concentric zones of equal area into which the pipe has to be divided in making measurements. The question therefore arises whether, when measurements are made by means of an anemometer, the instrument must be placed with its axis at the radii in question or at other points, the answer depending on whether or not the anemometer will rotate at the speed appropriate to the velocity of the filament of air at the centre of its disk or at a rate corresponding to some other wind speed.

Fig. 8.



In fig. 8 let $O1, O2, O3$, etc., represent the median lines of the eight blades of the anemometer (eight blades are almost invariably used) and let r be the radius to the centre of pressure of a blade. Let blade $O1$ be at an angle α to the reference line PQ , and let the velocity vary along PQ according to the relation

$$V = V_0(1 + Ax + Bx^2), \quad \dots \quad (15)$$

where V is the velocity at any point along PQ , distant x from P where the velocity is V_0 .

Also let $PO = OQ = r$.

Assuming the velocity distribution perpendicular to PQ to be uniform, *i.e.*, that the velocity at all points on a line perpendicular to PQ is the same, we can write down the velocities V_1, V_2 , etc., of the air impinging on the centre of

pressure of each blade as follows :—

$$\left. \begin{aligned} V_1 &= V_0 \left[1 + Ar(1 + \cos \alpha) + Br^2(1 + \cos \alpha)^2 \right], \\ V_2 &= V_0 \left[1 + Ar(1 + \cos \frac{\pi}{4} + \alpha) + Br^2(1 + \cos \frac{\pi}{4} + \alpha)^2 \right], \\ V_3 &= V_0 \left[1 + Ar(1 - \sin \alpha) + Br^2(1 - \sin \alpha)^2 \right], \\ V_4 &= V_0 \left[1 + Ar(1 - \sin \frac{\pi}{4} + \alpha) + Br^2(1 - \sin \frac{\pi}{4} + \alpha)^2 \right], \\ V_5 &= V_0 \left[1 + Ar(1 - \cos \alpha) + Br^2(1 - \cos \alpha)^2 \right], \\ V_6 &= V_0 \left[1 + Ar(1 - \cos \frac{\pi}{4} + \alpha) + Br^2(1 - \cos \frac{\pi}{4} + \alpha)^2 \right], \\ V_7 &= V_0 \left[1 + Ar(1 + \sin \alpha) + Br^2(1 + \sin \alpha)^2 \right], \\ V_8 &= V_0 \left[1 + Ar(1 + \sin \frac{\pi}{4} + \alpha) + Br^2(1 + \sin \frac{\pi}{4} + \alpha)^2 \right]. \end{aligned} \right\} (16)$$

Let the anemometer rotate under the effect of this variable velocity at a linear speed \bar{v} which would correspond, according to the calibration curve, to a wind speed \bar{V} . Then \bar{V} and \bar{v} will be such that the torque on the whole instrument rotating at this speed will be equal to the sum of the individual torques contributed by each blade.

Now from equation (3) we have

$$\text{Torque} = K\rho A\phi(V^2 + v^2)mr \cos(\theta - \phi + \gamma).$$

Provided that the wind speed is such that the anemometer is rotating at a fair speed, *i. e.*, that we are working on a portion of the calibration curve some distance from B in fig. 1, no appreciable error will be introduced by assuming that ϕ , and hence also K and γ , are constant for all the blades, so that we may write

$$\text{Torque} = K'm(V^2 + v^2).$$

The condition of total torque equal to sum of torques of all the blades is, therefore, expressed by the equation

$$8K'(\bar{V}^2 + \bar{v}^2) = K'\{V_1^2 + \bar{v}^2 + (V_2^2 + \bar{v}^2) + \dots + (V_8^2 + \bar{v}^2)\},$$

$$\text{i. e.,} \quad 8\bar{V}^2 = V_1^2 + V_2^2 + V_3^2 + \dots + V_8^2 = \Sigma V_i^2.$$

From equations (16) it will be found, after reduction, that

$$\Sigma V_1^2 = 8V_0^2 \left[(1 + Ar + Br^2)^2 + \frac{r^2}{8} (4A^2 + 8B + 24ABr + 27B^2r^2) \right],$$

which is independent of α and hence constant for all positions of the blades, so that

$$\bar{V} = V_0 \sqrt{(1 + Ar + Br^2)^2 + \frac{r^2}{8} (4A^2 + 8B + 24ABr + 27B^2r^2)}. \quad \dots (17)$$

In this equation \bar{V} is, as we have seen, the wind speed indicated by the anemometer. If the instrument indicated the speed of the wind passing through the centre of its disk, the value of \bar{V} would be $V_0(1 + Ar + Br^2)$, so that it appears that the indicated wind speed is the speed of the air at some point along the radius of the anemometer.

To get some idea of the magnitude of the discrepancy, we must take numerical examples. Let us assume, in order to fix our ideas, that the wind speed given by equation (15) is V_0 at $P(x = 0$ in fig. 8) and rises to $2V_0$ at $Q(x = 2r)$, and that at $x = r$, the centre of the disk, $V = 1.8V_0$. We can now calculate the values of A and B and, by inserting these in equation (17), we get

$$\bar{V} = 1.69V_0,$$

which is 6 per cent. less than the velocity at the centre of the disk, and is the velocity at the point $x = 0.81r$, instead of at $x = r$.

If the diameter of the anemometer is small compared with that of the pipe, it will probably be sufficiently accurate to assume a linear variation of velocity across the disk of the form

$$V = V_0(1 + Ar).$$

In this case, similar reasoning leads to the result

$$\bar{V} = V_0 \sqrt{(1 + Ar)^2 + \frac{A^2 r^2}{2}},$$

and, on the assumption, as before, that the velocity at $x = 2r$ is twice the velocity at $x = 0$, we have

$$\bar{V} = 1.54V_0 = \text{velocity at the point } x = 1.08r,$$

i. e., \bar{V} is 2-1/2 per cent. greater than the velocity at the centre of the disk.

In practice, provided the pipe diameter is reasonably large in relation to that of the anemometer, a distribution of velocity such as that assumed in both the above cases, in which the wind speed at the centre of pressure of a blade in one of its extreme positions is double its value in the other, is probably of very rare occurrence, so that in general the errors in indicated wind speed will be less than those given above.

4.1.

CONCLUSIONS.

The foregoing analysis serves to define the various conditions appropriate to the use of the vane anemometer, and to impose certain limitations thereon.

As regards the influence of a fluctuating wind speed, it would appear that no perceptible effect is normally to be anticipated from this cause. Judged by usual standards, a very unsteady wind speed would be required to cause the instrument to give readings markedly in excess of the mean speed.

Variations in the air density need be taken into account only when an instrument is used in the extreme lower end of its range for the measurement of very slow wind speeds. A statement of the air temperature and barometric pressure at which the instrument was tested should accompany the calibration curve of an anemometer intended for low speed work; the method of applying the necessary corrections is shown in the analysis.

It is important that instruments should be used only within the range for which they are intended. The ordinary anemometer is suitable neither for the measurement of very low wind speeds, nor for speeds in excess of about 50 feet per second. For the former work, special care in the design and construction is necessary if a satisfactory performance is to be obtained; reference has been made above to an instrument suitable for the measurement of low speeds. It is equally important that an anemometer should not be subjected to wind speeds higher than those for which it is designed; this point has already been emphasized in the introductory remarks of the present paper, see § 1.4.

The third problem which has been considered, namely the effect of a variation of wind speed across the anemometer disk, has an important bearing on measurements of air flow along pipes, where there is, in general, a variation in velocity across a section. It appears that, in order to avoid errors from this cause, the diameter of the anemometer should be

fairly small in comparison with that of the pipe, so that the variation of speed across the instrument itself is small. Unless precautions are taken to equalise the velocity at different points along the pipe diameter if a marked variation originally exists, an anemometer should not be used in a pipe whose diameter is less than about 7 or 8 times that of the instrument.

If the above limitations and conditions are observed, vane anemometers can be used with confidence to give all the accuracy that is ordinarily required. It should be remembered that, as with all measuring instruments, the vane anemometer has its particular sphere of usefulness, and it should consequently not be condemned because it cannot be used to measure wind speed in all circumstances; there must obviously be cases in which other instruments, the pitot-tube for example, will be more suitable. As an adjunct to the pitot-tube, the vane anemometer is a very valuable instrument, and for the measurement of very low wind speeds it would appear to provide the most convenient means available.

LXXXI. *On Irrotational Flow past Two Intersecting Planes.*
By W. B. MORTON, M.A., *Queen's University, Belfast* *.

IN a paper on the Electrification of two intersecting planes, published in this Magazine for February 1926 †, it was shown that if the complex variables $z\xi$ are connected by the equation

$$z = C\xi^{-1}(\xi - e^{i\alpha})^{1+k}(\xi - e^{-i\alpha})^{1-k},$$

then the perimeter of unit circle, on the ξ -plane, corresponds on the z -plane to the two sides of two straight lines of finite length making with each other the external angle $k\pi$. Other points of the z -plane are represented on the interior of the circle. The relation was found by integrating the Schwarz differential equation, regarding the two lines as a collapsed quadrilateral. In the present note the same transformation is used to investigate the irrotational steady motion of a liquid past the planes, without formation of dead water; or,

* Communicated by the Author.

† Vol. i. p. 337.

alternatively, the motion of the planes through liquid which is at rest at infinity. I have made drawings of the relative lines of flow for some directions in the particular case of two equal planes at right angles, the case which was examined in detail in the electrification problem. An expression is found for the couple exerted on the planes in the general case, and this is followed by a discussion of the positions of equilibrium of the planes relative to the stream, or of their possible steady motions through liquid.

The validity of the transformation given above can be verified by considering the variation of the argument of the expression in ζ as the point moves round the unit circle.

To make the values definite we lay it down that for points on the radii to $e^{i\alpha}$ and $e^{-i\alpha}$ the arguments of $(\zeta - e^{i\alpha})$ and $(\zeta - e^{-i\alpha})$ shall be $(-\pi + \alpha)$ and $(\pi - \alpha)$ respectively. The critical points are circumvented by small semi-circles drawn on the inner side of the circumference, and so their passage in the positive direction along the circle involves a decrease of π in the argument of the difference-terms. Thus the argument just before passing one of the points is $\frac{1}{2}\pi$ more than the value on the radius, and, just after passing it, $\frac{1}{2}\pi$ less. If ρ, ϕ are polar coordinates in the ζ -plane, and ϕ runs from $-\pi$ to π , we obtain, for points on the circle $\rho=1$,

$$\begin{aligned} \text{when } -\pi < \phi < \alpha, \quad \arg(\zeta - e^{i\alpha}) &= \frac{1}{2}(-\pi + \alpha + \phi) \\ \alpha < \phi < \pi, \quad &,, = \frac{1}{2}(-3\pi + \alpha + \phi), \end{aligned}$$

$$\begin{aligned} \text{when } -\pi < \phi < -\alpha, \quad \arg(\zeta - e^{-i\alpha}) &= \frac{1}{2}(3\pi - \alpha + \phi) \\ -\alpha < \phi < \pi, \quad &,, = \frac{1}{2}(\pi - \alpha + \phi). \end{aligned}$$

If the constant C is omitted, these values give for the argument of z the following:

$$\begin{aligned} -\pi < \phi < -\alpha, \quad \arg z &= (1 - 2k)\pi + k\alpha, \\ -\alpha < \phi < \alpha, \quad &,, = -k\pi + k\alpha, \\ \alpha < \phi < \pi, \quad &,, = -(1 + 2k)\pi + k\alpha. \end{aligned}$$

Put $C = Ae^{ik(\frac{3}{2}\pi - \alpha)}$ where A is real *, and the arguments become

$$\begin{aligned} (1 - \frac{1}{2}k)\pi \\ \frac{1}{2}k\pi \\ (1 - \frac{1}{2}k)\pi - 2\pi. \end{aligned}$$

By a slip this factor was given as $e^{ik\pi}$ in the former paper (top of p. 342). This did not affect the calculations for the symmetrical case for which $\alpha = \frac{1}{2}\pi$.

This gives two straight lines making an exterior angle $k\pi$ and placed so that the axis of η bisects their interior angle. The points $\phi = -\alpha$ and $\phi = \alpha$ on $\rho = 1$ correspond to the inside and outside of the corner.

For a point on the right-hand plane, $-\alpha < \phi < \alpha$, the distance from the angle

$$r = |z| = 4A \sin^{1+k} \frac{1}{2}(\alpha - \phi) \sin^{1-k} \frac{1}{2}(\alpha + \phi),$$

$$dr/d\phi = 2A \sin^k \frac{1}{2}(\alpha - \phi) \sin^{-k} \frac{1}{2}(\alpha + \phi) (\sin \phi + k \sin \alpha).$$

So r is maximum when $\sin \phi = -k \sin \alpha$. The end of the line therefore corresponds to the value $\phi = -\beta$, where $\sin \beta = k \sin \alpha$ and the length is

$$4A \sin^{1+k} \frac{1}{2}(\alpha + \beta) \sin^{1-k} \frac{1}{2}(\alpha - \beta).$$

For the end of the left-hand line we find in the same way $\phi = -(\pi - \beta)$ and the length

$$4A \cos^{1+k} \frac{1}{2}(\alpha - \beta) \cos^{1-k} \frac{1}{2}(\alpha + \beta).$$

The parameter α is therefore given by the ratio

$$\text{right-hand length/left-hand length}$$

$$= \tan \frac{1}{2}(\alpha + \beta) \tan \frac{1}{2}(\alpha - \beta) \{ \sin(\alpha + \beta) / \sin(\alpha - \beta) \}^k$$

with $\sin \beta = k \sin \alpha$.

Points near the origin on the ζ -plane correspond to distant points on the z -plane. As $\rho \rightarrow 0$ the arguments of $(\zeta - e^{i\alpha})$ and $(\zeta - e^{-i\alpha})$ for any ϕ approach the radial values already assigned, $(-\pi + \alpha)$ and $(\pi - \alpha)$ respectively. The argument of z approaches the value $-k(\frac{1}{2}\pi - \alpha) - \phi$ *.

This is the limiting inclination to the axis of x of the curve $\phi = \text{const.}$ The diagram given (*loc. cit.* p. 342) of the curves $\rho = \text{const.}$, and $\phi = \text{const.}$ for two equal lines at right-angles ($k = \frac{1}{2}$, $\alpha = \frac{1}{2}\pi$) can be taken to represent irrotational two-dimensional flow round two planes. We pass now to the question of steady flow past the planes.

Let u be the velocity potential and v the stream-function, and write $u + iv = w$. It is easy to show that the required

* Erroneously given as $k(2\alpha - \pi) - \phi$ in the former paper.

solution is given by the equation

$$w = B(e^{-i\gamma}\zeta + e^{i\gamma}\zeta^{-1})$$

with
$$z = A e^{-ik(\frac{1}{2} - \alpha)} \zeta^{-1} (\zeta - e^{i\alpha})^{1+k} (\zeta - e^{-i\alpha})^{1-k}.$$

Putting $\zeta = \rho e^{i\phi}$ and separating the real and imaginary parts of w , we have

$$u = B(\rho^{-1} + \rho) \cos(\phi - \gamma)$$

$$v = -B(\rho^{-1} - \rho) \sin(\phi - \gamma).$$

The stream-line $v=0$ is made up of the curve $\phi=\gamma$ and the two faces of the planes over which $\rho=1$. The direction of the undisturbed stream is thus $-k(\frac{1}{2}\pi - \alpha) - \gamma$.

We may find the distance at infinity between the stream-line $v=C$ and a parallel line drawn through the point of intersection of the planes. When ρ is small the approximate values are

$$|z| = A/\rho$$

$$\arg z = -k(\tfrac{1}{2}\pi - \alpha) - \phi - 2\rho(\cos \alpha \sin \phi - k \sin \alpha \cos \phi).$$

For a distant point on the line

$$-B(\rho^{-1} - \rho) \sin(\phi - \gamma) = C$$

we have
$$\phi = \gamma - CB^{-1}\rho.$$

It follows that the required distance is

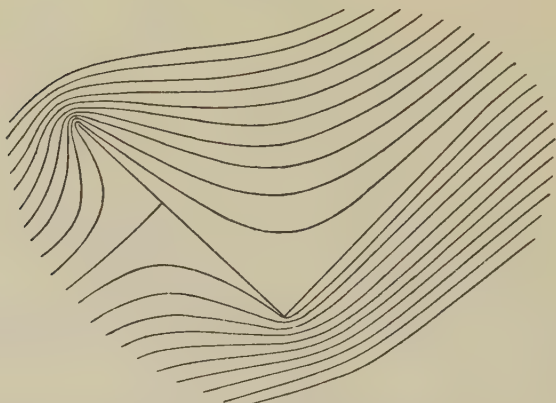
$$ACB^{-1} + 2A(k \sin \alpha \cos \gamma - \cos \alpha \sin \gamma).$$

The calculation of the coordinates of points on the stream-line $v=C$ is laborious, but a sufficiently accurate drawing of the curves of flow can be made by calculating values of ϕ for a succession of values of ρ and plotting directly on tracing-paper laid over the network of coordinate lines $\rho=\text{const.}$ and $\phi=\text{const.}$ as drawn to represent equipotentials and lines of force in the electrification problem.

I have drawn the lines of flow for a number of directions past two equal planes at right-angles, using the diagram of the previous paper as a basis. It will be sufficient to reproduce one case (fig. 1), that for a stream whose direction at infinity makes 30° with the axis of x . It will be noticed that the stream splits at the edge of the planes, although the

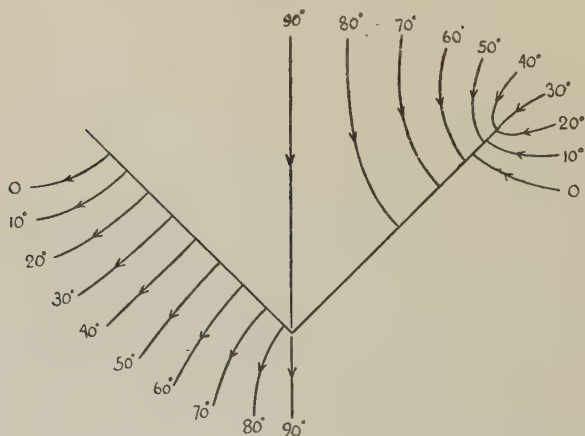
limiting direction of the stream makes an angle of 15° with the plane. The other cases present similar features as

Fig. 1.



regards the general arrangement of the stream-lines. Fig. 2 shows the points where the stream splits on the two planes

Fig. 2.



for different directions of flow. The arrows can, of course, be reversed.

If q is the velocity at any point then q^{-1} is the modulus,

and the inclination of q to the real axis the argument, of the complex quantity

$$\begin{aligned} dz/dw &= dz/d\zeta \times d\zeta/dw \\ &= A e^{ik(\frac{3}{2}\pi - \alpha)} (\zeta - e^{i\alpha})^k (\zeta - e^{-i\alpha})^{-k} \\ &\quad \times (\zeta + e^{i\beta}) (\zeta - e^{-i\beta}) / B \zeta (e^{-i\gamma} \zeta - e^{i\gamma} \zeta^{-1}). \end{aligned}$$

Putting $\zeta=0$, we see that the undisturbed velocity of the stream is $B/A=q_0$ say, and its direction is that of the line $\phi=\gamma$ at infinity, i. e., $-k(\frac{1}{2}\pi - \alpha) - \gamma$.

For points on the planes ($\rho=1$) we find

$$q = q_0 \left| \sin(\phi - \gamma) \cdot \sin^{\frac{k}{2}}(\phi + \alpha) \cdot \sin^{-\frac{k}{2}}(\phi - \alpha) \cdot (\sin \phi + \sin \beta)^{-1} \right|.$$

This vanishes at $\phi=\gamma$ and $\phi=-\pi+\gamma$, where the streamline splits on the planes, and at $\phi=\alpha$ the inside of the corner. It is infinite at $\phi=-\alpha$, the outside of the corner, and at $\phi=-\beta$, $\phi=-\pi+\beta$, the tips of the planes.

When the forces exerted on the planes by the liquid are considered a result is found which at first sight seems to contradict the general theorem that a solid, in an irrotationally moving steady stream, without formation of dead water, is subject to a couple only. If the thrusts of the liquid on the planes act perpendicularly to them, it is evident that their resultant can vanish only when the two thrusts vanish separately. An examination of the integrals of the pressure as given by the above theory shows that this is not the case; so a definite resultant force appears to be exerted by the stream.

Without going into the integral expressions it is easy to see that the separate thrusts do not vanish by considering the limiting case, when the two planes flatten out into a single plane as k becomes zero. The points on the inner and outer sides of the angle then become opposite points on the two faces of the single plane which divide its breadth in the ratio $(1 - \cos \alpha)$ to $(1 + \cos \alpha)$. Obviously the thrusts on the two portions do not separately vanish for all values of α , and we are justified by considerations of continuity in inferring that the same is true when the two parts are inclined. In the case of a single plane the thrusts on the two parts are equal and opposite, and being parallel they form a couple, but in the case we are considering there is not this way of escape from a resultant force.

The explanation of the paradox is of course to be sought

in the infinite velocities at the edges of the planes. The double plane is to be regarded as the limit approached by the boomerang-like figure, with rounded ends, formed by a closely fitting equipotential in the electrification problem. On the ends there will be a thrust, or rather defect of thrust, directed along the planes due to the high velocity round the ends. As the edges are sharpened into the planes these thrust-components do not vanish but approach a definite limit. There are thus forces along the planes which balance the forces on their faces, in accordance with the general dynamical theory.

By way of illustration of this point it will be sufficient to consider the well-known case of an elliptic cylinder as it shrinks to the plane strip between its foci. It is easy to show that, when the stream is oblique to the major axis, the component thrust-defect on each half of the section, in the direction of the major axis, approaches a finite limit.

We have $q^2 = q_0^2 e^{2\alpha} \sin^2(\eta - \gamma) / (\cosh^2 \alpha - \cosh^2 \eta)$,

where q_0 is the velocity of the undisturbed stream, γ its inclination to the major axis, $(\alpha \cosh \alpha, \alpha \sinh \alpha)$ the axes of the ellipse and η the excentric angle of a point on it. For the component along Ox of the thrust-defect on one side of the minor axis the value found is

$$\begin{aligned} & \frac{1}{2} \rho q_0^2 \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} e^{2\alpha} \sinh \alpha \sin^2(\eta - \gamma) \cos \eta \, d\eta / (\cosh^2 \alpha - \cosh^2 \eta) \\ &= \rho q_0^2 e^{2\alpha} \{ \cos 2\gamma \sinh \alpha + (\sin^2 \gamma \cosh^2 \alpha \\ & \quad - \cos^2 \gamma \sinh^2 \alpha) \tan^{-1} \operatorname{cosech} \alpha \}; \end{aligned}$$

when $\alpha=0$ this becomes $\frac{1}{2} \pi \rho q_0^2 \sin^2 \gamma$, so a plane strip set obliquely in a stream is subject to a kind of hydrodynamical tension along its edges.

The couple acting on the planes can be found by taking the moments of the normal pressures round the angle. The extra forces, which have been invoked to get rid of the resultant force, pass through the intersection of the planes and so give no moment. Consider an element dr on the lower surface of the right-hand plane, where ϕ lies between α and $-\beta$; its contribution to the torque, in the positive

direction, is

$$-\frac{1}{2}\rho q^2 r dr \\ = -2A^2 \rho q_0^2 \sin^2(\phi - \gamma)(\cos \phi - \cos \alpha) d\phi / (\sin \phi + \sin \beta).$$

The disappearance of the index k , except in so far as it is involved in $\sin \beta = k \sin \alpha$, is rather surprising here, and makes it possible to integrate the expression.

It will be noticed that the formula for the element of torque gives the correct sign throughout the entire range of ϕ from $-\pi$ to π .

$$\begin{array}{ll} \text{It is} & + \text{ for } -\pi < \phi < -(\pi - \beta) \\ & - \text{ ,, } -(\pi - \beta) < \phi < -\alpha \\ & + \text{ ,, } -\alpha < \phi < -\beta \\ & - \text{ ,, } -\beta < \phi < \alpha \\ & + \text{ ,, } \alpha < \phi < \pi, \end{array}$$

in each case opposite to the sense of the moment of the pressure on the corresponding part of the planes

Evaluation of the indefinite integral gives

$$\begin{aligned} & 2 \int \sin^2(\phi - \gamma)(\cos \phi - \cos \alpha) d\phi / (\sin \phi + \sin \beta) \\ & = -(\cos 2\beta \sin 2\gamma - 2 \cos \alpha \sin \beta \cos 2\gamma) \phi \\ & \quad + 2(\cos \alpha \sin 2\gamma - \sin \beta \cos 2\gamma) \sin \phi \\ & \quad + \cos 2\gamma \sin^2 \phi + 2(\sin \beta \sin 2\gamma \\ & \quad + \cos \alpha \cos 2\gamma) \cos \phi - \sin 2\gamma \sin \phi \cos \phi \\ & \quad + 2 \sec \beta \{ (\cos \beta - \cos \alpha) \sin^2(\beta + \gamma) \log \sin \frac{1}{2}(\phi + \beta) \\ & \quad + (\cos \beta + \cos \alpha) \sin^2(\beta - \gamma) \log \cos \frac{1}{2}(\phi - \beta) \}. \end{aligned}$$

When the range of integration includes one of the edges $\phi = -\beta$, $\phi = -(\pi - \beta)$, there is physical justification for taking the principal value of the improper integral.

For the two planes taken together, with limits $\pm\pi$, the torque is

$$2\pi A^2 \rho q_0^2 (\cos 2\beta \sin 2\gamma - k \sin 2\alpha \cos 2\gamma)$$

with positive sense, *i. e.* counter-clockwise.

When the two planes are flattened out into one, $k=0$, $\beta=0$, the breadth $=4A$ and the moment $=2\pi A^2 \rho q_0^2 \sin 2\gamma$. This agrees with the known result for the case of an elliptic cylinder reduced to a lamina, *viz.*, $\frac{1}{2}\pi \rho q_0^2 c^2 \sin 2\gamma$.

It will be seen that the torque in every case varies with the angular position of the planes in the usual "quadrantal" manner, the amplitude, or maximum value being

$$2\pi A^2 \rho q_0^2 (\cos^2 2\beta + k^2 \sin^2 2\alpha)^{\frac{1}{2}} \\ = 2\pi A^2 \rho q_0^2 \{1 - 4k^2(1 - k^2) \sin^4 \alpha\}^{\frac{1}{2}}.$$

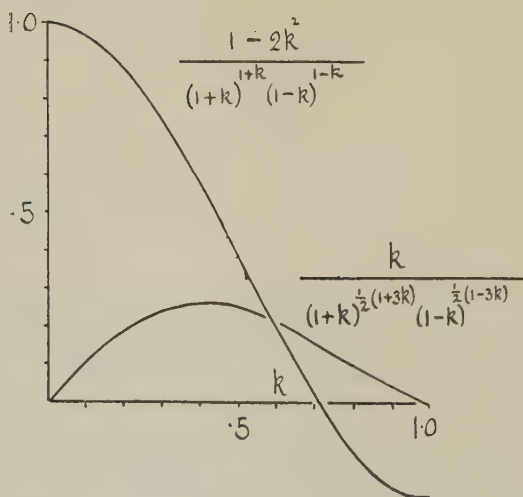
In general A, α are complicated functions of the dimensions of the planes together with the angle $k\pi$. Explicit formulæ can be got when the breadths are equal, for then $\alpha = \frac{1}{2}\pi$, $\beta = \sin^{-1} k$, γ is the inclination of the stream to the exterior bisector of the angle, the breadth of either plane is

$$2A(1+k)^{\frac{1}{2}(1+k)} \cdot (1-k)^{\frac{1}{2}(1-k)} = a, \text{ say,}$$

and the torque is

$$2\pi A^2 \rho q_0^2 (1 - 2k^2) \sin 2\gamma \\ = \frac{1}{2} \pi a^2 \rho q_0^2 \sin 2\gamma \cdot (1 - 2k^2) / (1+k)^{1+k} (1-k)^{1-k}.$$

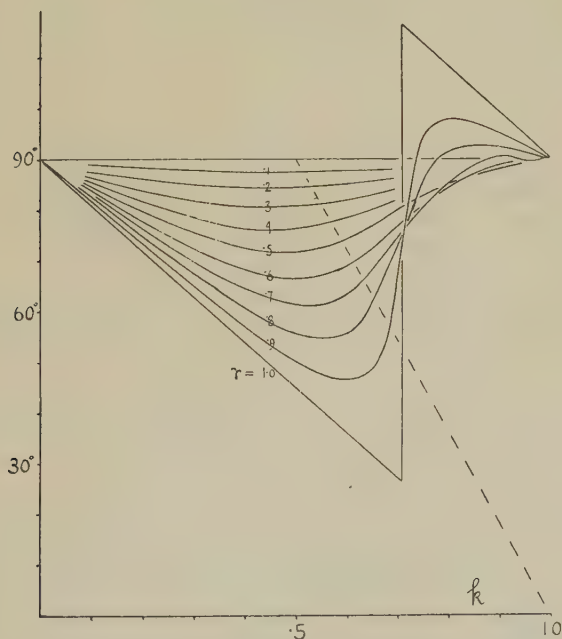
Fig. 3.



The course of the function of k is shown on fig. 3, which therefore gives the variation of the maximum couple for equal planes of given dimensions as the angle between them is changed. The torque vanishes for the symmetrical positions

$\gamma=0$ and $\gamma=\frac{1}{2}\pi$, the planes are then in equilibrium relative to the stream. Examination of the sense of the couple shows that the equilibrium is stable when the direction of the stream coincides with the interior bisector of the angle, for $k < \frac{1}{\sqrt{2}}$, with the exterior bisector for $k > \frac{1}{\sqrt{2}}$. This illustrates the general tendency of a body to set its long dimension across the stream. Evidently, as the planes are shut up together from a wide-spread angle, we must pass from one configuration to the other. The critical form is reached

Fig. 4.



when the planes make an acute angle of about $52^{\circ}8$. The planes will then remain indifferently in any posture relative to the stream. It is only when the planes are equal that this curious state of affairs is found. With unequal breadths there is always one definite position of stable relative equilibrium in the stream, with an unstable position at right angles to it.

The way in which this position varies with the inclination of the planes and the ratio of their breadths is shown on fig. 4. It is more convenient, in discussing the matter, to

regard the planes as moving steadily through a quiescent liquid. Each curve on the figure refers to a definite breadth ratio, from 0·1 to unity. The abscissa is the exterior angle between the planes, $k\pi$, while the ordinate is the inclination to the larger plane of the stable direction of steady translation through the liquid, viz. $(\frac{1}{2}\pi - k\alpha + \gamma)$, where γ is taken as acute. To obtain these curves another set was first plotted in which each curve corresponded to a given value of k , and the direction of motion was plotted against the breadth-ratio for a succession of values of the angle α . From these the direction-angle was then read off at the points where the ordinate corresponding to any breadth-ratio crosses the series of curves, and so the material for fig. 4 was obtained.

The straight-line graph shows the case of equal planes with the sudden change from the internal to the external bisector at external angle $\pi/\sqrt{2}$. When the length of one plane is slightly decreased this discontinuity passes into a very rapid change of orientation in the neighbourhood of the same angle. With still smaller lengths of the second plane the graph ceases to rise above the 90° level. If we begin with the two planes in line ($k=0$), and rotate the smaller plane, the direction of steady translation first rotates in the same direction and then returns to the normal position. There are two special cases of some interest :

(1) The points where the curves are met by the broken line whose ordinate is $(1-k)\pi$ correspond to stable translation in the direction of the shorter plane. It will be seen that this is possible for any breadth-ratio.

(2) If the curve for an assigned ratio intersects the level of 90° there is steady translation in the direction normal to the larger plane, just as if the other were not attached. We have then $\gamma=k\alpha$, and the equation connecting k and α becomes

$$k \sin 2\alpha - \tan 2k\alpha(1 - 2k^2 \sin^2 \alpha) = 0.$$

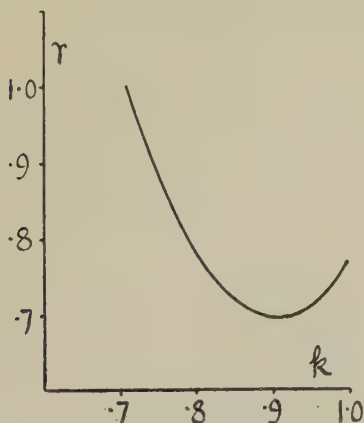
The assumed motion occurs when this equation for k has a root between 0 and 1. For $\alpha < \frac{1}{4}\pi$ the left-hand side is negative and finite throughout the range. For $\alpha > \frac{1}{4}\pi$ it changes sign through infinity from negative to positive at $k = \pi/4\alpha$. There will be a root between this value and $k=1$ provided the differential of the expression with respect to k

is positive at $k=1$, i. e., if

$$\sec 2\alpha(4 \sin 2\alpha - \sin 4\alpha - 4\alpha) > 0.$$

The expression in brackets vanishes for $\alpha=61^\circ.3$ approximately. For this value of α the third root coincides with $k=1$, and as α increases to 90° the root moves back to $1/\sqrt{2}=0.707$. The corresponding values of the breadth-ratio, r , are $.77$ and unity, but r does not increase continuously from the former to the latter value as the associated values (αk) move continuously from $(61^\circ.3, 1)$ to $(90^\circ, .707)$. The complicated nature of the connexions between r, k, α , makes it necessary to examine the matter arithmetically. When this is done it is found that r sinks to a minimum of about $.69$ for $\alpha=67^\circ$, $r=.91$, approxi-

Fig. 5.



mately. The connexion between k and r is shown on fig. 5.

We can now describe the course followed by the curves of fig. 4 at their right-hand ends. The curve for $r=.69$ is bent upwards to touch the lower side of the 90° level at about $k=.91$. Curves for higher values break through this level, there being two intersections up to $r=.77$ and one for r between $.77$ and unity. This means that for breadth-ratios between $.69$ and $.77$ there are two inclinations of the planes which give steady translation perpendicular to the larger

plane, above .77 there is one inclination, and below .69 none.

The scheme of a broad plane, moving in its own direction, with a short plane attached to it at an angle, suggests a simplified model of a ship and rudder. It is perhaps worth while to point out the complete lack of similarity in the actions in the two cases. If in our ideal case we began with the two planes in line and moving with unstable steady motion in their own direction, a slight deflexion of the rudder-plane will cause the whole to swing into the stable direction, nearly perpendicular to the large plane. The turning will be through the acute angle, and this is in the direction opposite to that in which a rudder turns a ship. Further, the torque will be in the same direction whether the motion is ahead or astern.

An expression can be found for the torque at any angle when the rudder-plane is a small fraction of the breadth of the other, in this case the parameter α is small, $\beta = k\alpha$, and γ is also $=k\alpha$ when the motion is along the larger plane, for then

$$-\gamma - k(\tfrac{1}{2}\pi - \alpha) = -\tfrac{1}{2}k\pi.$$

We find the following approximations :

Breadth of large plane $= 4A = a$ say.

Breadth of small plane $= A(1+k)^{1+k}(1-k)^{1+k}\alpha^2 = b$.

Torque $= A^2 \rho q_0^{2/3} \pi k (1-k^2) \alpha^3$.

Eliminating A, α we find the torque

$$= \frac{2}{3} \pi \rho q_0^2 a^{\frac{1}{2}} b^{\frac{3}{2}} \cdot k / (1+k)^{\frac{1}{2}(1+3k)} \cdot (1-k)^{\frac{1}{2}(1-3k)}.$$

This function of k is plotted on fig. 3.

It remains to try the effect of superposing a circulation on the simple flow discussed in the present paper, on the lines which have, in the hands of Prandtl and others, led to important developments in the theory of the aeroplane.

LXXXII. *Alternative Currents in Rarefied Oxygen in the same Circuit.* By Rev. P. J. KIRKBY, D.Sc.*

Introduction.

1. **I**N 'Nature,' Aug. 19th, 1922, I gave a preliminary account of certain peculiar effects in the electric discharge of oxygen. They were observed in the course of a further investigation into the nature of those discontinuities in the electric discharge through oxygen at pressures close to $\cdot 8$ mm., about which I published an account in the *Philosophical Magazine* of April 1908. The latter effects were exhibited in that region of a long cylindrical discharge which is known as the positive column.

The positive column in oxygen at pressures of the order $\cdot 8$ mm., with which these researches are chiefly concerned, occupies the whole length of the discharge with the exception of the first five to eight cm. from the cathode (or negative electrode). Thus in a discharge-tube where the electrodes are 20 cm. apart, the column appears as a uniform pale pink cylinder, about 13 cm. long at the pressure $\cdot 8$ mm., terminating at the anode or positive electrode. In oxygen striæ, which in other gases present such a striking appearance, do not often appear, at least at our pressures: when they did, they were close together and entirely unlike those of other gases.

2. Within this luminous positive column the *electric force* (fall of voltage per cm.) along the length of the tube is constant; and it is here that the discontinuities described in the *Phil. Mag.* of Feb. 1908 were observed. They were of the following nature:—As the pressure was raised from $\cdot 53$ to $\cdot 8$ mm., it was found that the electric force rose with perfect regularity in arithmetical progression with equal increments of pressure from 14·4 to 21·4 volts per cm.; after which an imperceptible increase of pressure brought about a radical change in the discharge, so that the electric force within the positive column was reduced to about 11 volts per cm. Moreover, this discontinuity was a reversible effect: namely, a very slight decrease of pressure caused the electric force to jump back to about 20 volts per cm., indicating the recovery of the previous state of the discharge. It should be added that when the pressure was increased beyond the discontinuity value of about $\cdot 8$ mm., the same force was observed

* Communicated by the Author.

to decrease rapidly to a minimum of about 4·5 volts per cm. (at a pressure between 1·5 and 2 mm.), after which it increased with the pressure.

3. The experiments to be described in this paper show that the reversible effect just alluded to, produced by an imperceptible change of pressure, can be produced without any change of pressure, and not merely at one definite pressure, but at any pressure within a certain region of pressure, of which ·8 mm. is about the centre. Thus if the pressure of oxygen in a discharge-tube, *forming part of a fixed circuit*, falls within that region of pressure (so far observed to be ·54 to 1·04 mm.) two different discharges are producible, one characterized by a positive column with high electric force, the other characterized chiefly by a positive column of much smaller electric force.

Ordinary and Extraordinary Currents defined.

4. Since it is necessary frequently to distinguish between these two types of current, I propose to call the former of these alternative discharges, namely the one with the high electric force in its positive column, the *ordinary current* (or discharge, etc.), and the other the *extraordinary current*, borrowing these adjectives from the terminology of double refraction. For the ordinary currents are very regular: they are analogous to currents of similar magnitude and at similar pressures through hydrogen and nitrogen, having electric forces in their positive columns of the same order of magnitude with those gases. (See section 18.) And on the other hand, the extraordinary discharges appear to be *sui generis*.

5. In addition to having an abnormally small force in its positive column the extraordinary current in a given circuit is distinguished from the ordinary by its greater value, and also by its positive column being somewhat longer (about 1 cm.) than that of the ordinary, and also somewhat paler in colour.

Further, in contrast with the ordinary current, the extraordinary has a tendency to disturbance by the passage of electricity, being perhaps more sensitive to the presence of ozone. Thus if the discharge is made to alternate several times between the ordinary and extraordinary currents, the latter will exhibit a slight progressive modification, while the ordinary will remain unchanged.

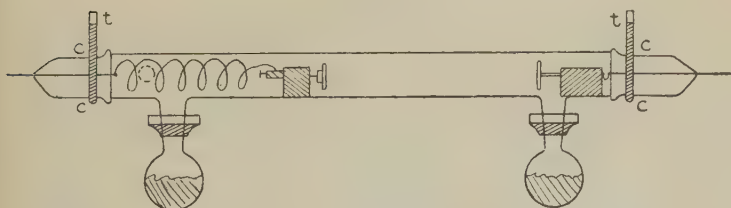
The Experiments.

6. The experiments consisted in passing a steady current through a discharge-tube between two circular electrodes, of which the anode was movable so that the length of the discharge could be varied. The current came from a battery of small accumulators of 1020 volts or less, and passed through a high resistance which could be varied up to two megohms. By this means it was possible to study currents of various length and magnitude and to determine their electric forces in the positive column.

The Discharge-tube.

7. This is shown in elevation (projection on a vertical plane through the tube's axis), and drawn to scale, in fig. 1. A cylindrical tube of nearly 48.5 cm. length and 2.8 cm. internal diameter (3.1 external diam.) was closed at both ends by airtight glass caps, through which protruded thick platinum wires fused to them. The platinum wires were attached to stiff silver wires passing through the interior of the caps, and connected by thin wires to the electrodes.

Fig. 1.



The caps were designed to make a perfectly gas-tight fit to the ends of the glass tube, which was slightly inclined as each end to receive them. A narrow side-tube (*t*, fig. 1) was fused to each cap, and a small circular protuberance, containing the base of this tube, was blown round the cap, forming with the outer surface of the discharge-tube, with the cap fitted on, a little circular canal (*c, c*), into which the side-tube opened. The internal surface of each cap on both sides of the circular canal was ground to fit its end of the discharge-tube, which was also ground. By using vaseline optical contact was then secured between the caps and the tube; and mercury was poured into the side-tube (*t*), filling the canal and part of the side-tube itself (as shown in fig. 1).

The side-tubes being vertical and about 4 cm. high, when they were more or less full of mercury the mercury within the canals had everywhere a pressure greater than atmospheric pressure, and was therefore able to stop any air that would have been otherwise forced by the pressure of the atmosphere between the tube and the cap.

By this means, notwithstanding the large extent of the surfaces of contact exposed to possible air-leaks, not the slightest leak was ever observed through the discharge-tube, even after weeks at a time, though a leak of less than .001 mm. was detectable by the particular form of McLeod gauge that I employed. The caps could be taken off without letting mercury into the apparatus by inverting them, to allow the mercury to run out of the canals, before taking them off.

The small bulbs below the tube in fig. 1 are drying vessels containing phosphorus pentoxide, about 5 cm. in diameter. They were ground to fit the small vertical tubes blown into the main discharge-tube, and carried mercury cups, thus obviating any air-leak. This apparatus was made to my design by Messrs. J. J. Griffin, Kingsway, London.

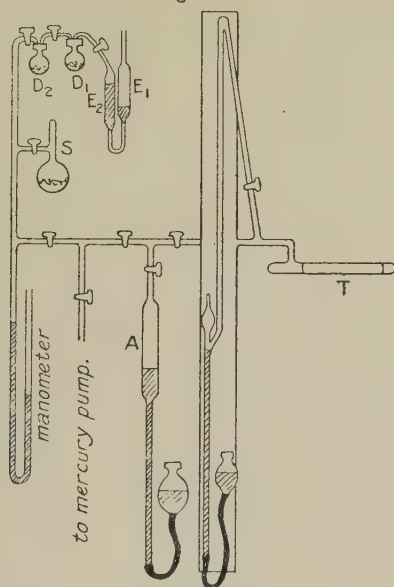
Electrodes.

8. The electrodes were made of pure gold .25 mm. thick, backed by pure silver .75 mm. thick, to exclude oxidation. They were fixed to small solid iron carriers, capable of sliding along the discharge-tube, and connected by fine wires to the silver continuations of the platinum wires which protruded through the glass caps. By means of an electromagnet outside the discharge-tube the electrodes could thus be moved along it into any desired position. The cathode only needed slight adjustments. But the anode was connected to the negative terminal by a long thin coiled copper wire; and later on by a thin brass wire. As the anode was moved back by the electromagnet, the thin wire coiled itself behind it, so that it was easy to adjust the anode to any distance from the cathode. The diameter of the anode was 2 cm. That of the cathode was at first 2.4 cm.; but after a number of experiments one of the caps was accidentally broken and the opportunity was taken to replace the cathode by a similar one of 2.75 cm. diameter, which fitted the tube closely in the reconstructed apparatus. These pure gold and silver electrodes were supplied by Messrs. Matthey and Johnson.

Preparation of the Oxygen for the Experiments.

9. The scheme of the whole apparatus is sufficiently indicated by the diagram of fig. 2. The oxygen was produced by electrolysis of sodium hydrate in the tube E_2 . The tube E_1 opens into the air through a tube (not shown in the figure) full of powdered caustic potash, to prevent any carbon dioxide from entering into the electrolyte as the air is drawn into E_1 . The oxygen was dried in D_1 , D_2 over phosphorus pentoxide, and passed into the reservoir S , containing the same substance, from which it passed into the

Fig. 2.



discharge-tube T , the McLeod gauge, and the vessel A . A had a capacity commensurate with that of the discharge-tube and McLeod gauge together. Its long barrel was provided with a scale, so that by raising or lowering the mercury by the necessary amount, the proper taps open, the pressure in T could be adjusted accurately. It was also easy by means of this barrel, its cross-section known, to ascertain the joint capacity of T and the McLeod gauge.

All the connexions of the apparatus were of fused glass. No rubber was used except for working the mercury pump, A , and the McLeod gauge; and the lower junction of the

rubber with the glass on this gauge was in a glass full of mercury. All the taps had mercury cups.

The whole of the apparatus, with all the taps open, was then exhausted to a low pressure and thoroughly tested for airtightness, and the electrolyte in E_2 was drawn up to the tap before the generation of oxygen. These precautions guaranteed the oxygen to be of a high degree of purity. It entered the discharge-tube by a horizontal side-tube blown into the former, as indicated by the little dotted circle of fig. 1, near the left cap.

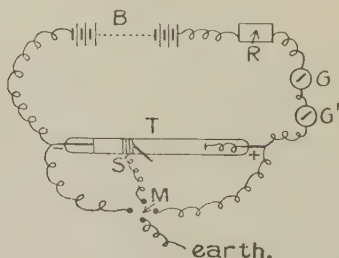
Method of Experiment.

10. The method eventually used for examining the alternative discharges producible in the discharge-tube, without any alteration in the electric circuit containing it or in the mass of the oxygen in that tube, was as follows:—

A strip of tinfoil of about 3 cm. width was wrapped round the discharge-tube, forming a short cylinder. It was placed at such a distance from the cathode that the positive column just about entered the cylinder. If now this ring, or little cylinder, is connected with the anode, the larger or extraordinary current will pass in general, and will continue if the ring is insulated. But if the ring is connected to the cathode, the smaller or ordinary current will pass and will continue after insulating the ring.

This ring of tinfoil was subsequently replaced by a ring, S, consisting of four turns of fairly thick copper wire, bent round the discharge-tube and in contact with it, so as to have a width of about one cm. It was attached to a vulcanite handle, by which it could be moved to any required position on the tube.

Fig. 3.



11. Figure 3 shows the electrical arrangements. The battery B maintained a steady current, determined by the resistance R, through the discharge-tube T. G was a high

resistance voltmeter (36,240 ohms) used as a galvanometer, capable of measuring currents exceeding .2 milliampere, and G' a still more sensitive one, which confirmed the smallest readings of G . M is a block of paraffin, having four small holes filled with mercury, by which the ring S could be immediately earthed or connected with anode or cathode. This method was used as the simplest way of charging the ring S positive or negative to an adequate potential. The circuit was well insulated for the purpose in view.

Determination of the Electric Force in the Positive Column.

12. The uniform electric force in the positive column was determined by a method which I have often used in other * researches, and which is free from the serious objection to the use of exploring wires in the discharge that they disturb the natural electrostatic field of the discharge.

The electrodes being at a distance D apart, a current C is passed from a battery B through a resistance R (one or two megohms), adjusted to give a suitable value to C . The anode is then moved through a distance d cm. nearer the cathode and B is reduced to $B-b$, R being unchanged and b being such that the current C is unchanged. Then the electric force is b/d volts per cm., provided that the two discharges are long enough to have positive columns. The validity of this method is easily proved by the constancy of b/d , when B , R , C remain constant. In practice it is difficult to hit exactly on b , the number of volts by which to reduce the battery so as to reproduce the previous current C when the anode has been moved through the distance d towards the cathode. And it is not necessary. For it is easy to obtain two adjacent values of b giving currents slightly greater and less than C , and then by interpolation to determine b precisely. The errors inherent in this method are a small percentage, unless the force in the positive column is small, in which case the errors are greater. Usually I took d to be about 1 cm. less than the length of the positive column; and having determined the electric force therein, I confirmed the result by a second observation in which d was half its previous value.

Another method, depending on the fact that the potential difference of the electrodes is practically independent of the current provided the range of variation of the current is restricted, is used below. (Sections 34 ff.)

* P. J. Kirkby, Phil. Mag. March 1907, April 1908; Proc. Roy. Soc. A, lxxxv. p. 151.

Preliminary Tables.

13. Before dealing with the experiments which exhibit the alternative discharges through oxygen with a fixed circuit, I give some tables which will illustrate the great difference of the electric forces in the positive columns of the two types of current, the ordinary and the extraordinary, and the abrupt transition which the discharge makes, when it is not controlled, at a certain critical pressure, which is not absolutely fixed but depends on the magnitude of the current and the condition of the gas, lying within, or adjacent to, the range of pressure $\cdot 6$ to $\cdot 8$ mm.

The values of Y in Table I. were obtained from many different masses of oxygen by the method described above, at the pressure and with the current (to the left of the Y) stated on the same line. The current was not controlled: whether it was the ordinary or the extraordinary was a matter of self-determination. It is, however, easy to distinguish the ordinary from the extraordinary by the greater value of Y , characteristic of the former, at the same or neighbouring pressures.

14. The table exhibits the currents at pressures of $\cdot 67$ mm. and below as ordinary, and currents at pressures of $\cdot 9$ mm. and above as extraordinary. At pressures between these figures, the nature of the current depends on its magnitude: the smaller the current, the higher the pressure at which it appears spontaneously as ordinary, and *vice versa*.

To save space and to facilitate comparison between the Y 's of currents which differ by a substantial fraction of a milli-ampere, the results are given in three double columns, which contain currents of about the same magnitude, namely, within 20 per cent. of $\cdot 25$ m.a., of $\cdot 47$ m.a., and of $1\cdot 25$ m.a., respectively. This is indicated at the head of each double column.

A comparison of the values of Y in the second and third double column, at the pressures $\cdot 48$, $\cdot 34$, $\cdot 23$ mm., indicates that an increase of $\cdot 74$ m.a. in the current goes with a *decrease* in Y of $1\cdot 2$ volts/cm. If, then, we assume that Herz's well-known rule* for similar discharges in nitrogen and hydrogen, namely, that in a given tube the concomitant increase in current and decrease in Y are in a constant ratio—if we assume that such a rule applies to the *ordinary* discharges of oxygen, we may conclude that the correction to be applied to the Y of any current C of these orders of

* Herz, *Wied. Ann.* liv. p. 244 (1895), or, Sir J. J. Thomson, 'Conduction of Electricity through Gases,' 1903, p. 456.

magnitude, in order to get the Y of a smaller current, $c-c$, m.a., is plus $1.6c$ volts per cm. (The corresponding correction for nitrogen discharges in our tube would be just twice as much.)

TABLE I.

p =the pressure of oxygen in mm.

C =the current in milliamperes.

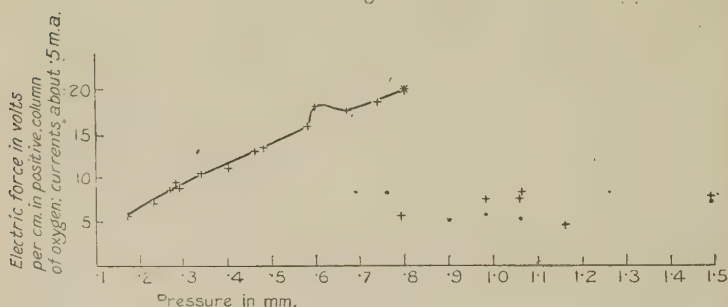
Y =electric force in the positive column in volts per cm.

p .	$C > .2$ m.a. $< .31$ "		$C > .38$ m.a. $< .57$ "		$C > 1.1$ m.a. < 1.43 "	
	C	Y	C	Y	C	Y
1.495	7.8	1.4	7.3
1.1654	4.6		
1.06495	8.1	1.36	5.25
1.06525	7.6	1.39	5.15
.9847	7.5	1.41	5.8
.9	1.43	5.0
.81201	20				
.81256	20.3				
.7957	5.7		
.78304	19.5				
.76	1.33	8.2
.74414	18.6		
.69	1.3	8.3
.67382	17.6		
.6216	18.8	.42	18.0		
.585	15.8		
.57	1.1	13.3
.4845	13.4	1.16	12.0
.46218	13.6				
.4625	14.4	.47	13.0		
.4256	11.4	.47	11.1		
.34495	10.6	1.23	9.4
.29495	9.0		
.28267	10.1	.48	9.5		
.27247	10.3	.453	8.7	1.06	8.3
.2352	7.0	1.29	5.8
.1647	5.3		

This result is in agreement with Table I. For if we plot the Y 's of the ordinary currents in the second double column of that table against the pressures, the points determine a

locus, the slight difference between the various currents in that double column and their mean, $\cdot 47$, producing an imperceptible effect in the corresponding Y 's. This is shown in fig. 4, in which the points thus determined are shown by a cross. It is also clear that the points whose coordinates are p , Y , from the first double column of Table I., fall very nearly on the locus of fig. 4, and that the slight correction of $1\cdot6c$, mentioned above, though not so insignificant as before, improves the approximation. But I have not complicated the figure of the locus by adding points from the other columns, except one (the star, $p = \cdot 81$, $Y = 20$) from the first double column.

Fig. 4.



15. A curious feature of the locus is produced by the value of $Y = 18$, at the pressure $\cdot 6$. If this is suppressed, the locus is a smooth curve (of continuous curvature). But I have found it impossible to do this, and to regard it condemned, as exceptionally erroneous, by the other observations, because no result seems more repeatedly confirmed. (See Table V.) It seems therefore necessary to conclude that there is a singularity here in the locus, the electric force making a sudden increase in value, after which it remains more or less constant while the pressure rises to about $\cdot 74$. If this is so, it is obviously connected with the exceptionally unstable nature of the oxygen in the immediate neighbourhood of this pressure.

The ordinary discharges appear thus to be as congruent among themselves in respect of their positive columns as the discharge of other gases. The values of the electric force in those columns are determinate and easily repeatable. Apart from the seeming anomaly alluded to above, their only distinguishing feature is the big rate of increase of the force per mm. rise of pressure, the current being constant. This

quantity, dY/dp , the slope of the curve of fig. 4, is, *e. g.* 70 per cent. greater than that of a similar curve for hydrogen.

16. The extraordinary discharges, on the other hand, have positive columns of very different characteristics. For not only is the electric force of a different degree of magnitude, but the discrepancies in their values cannot be accounted for by errors of observation. There is evidently a disturbing factor, which makes it difficult to reproduce an extraordinary current with the same precision which characterizes the ordinary. This fortuitous element will be discussed later.

The electric forces in the extraordinary positive columns, given in Table I., are represented in fig. 4 by isolated points, marked by crosses or dots according as the force is to be found in the second or the third double column. All these values of Y fall within the parallel lines,

$$Y = 6.4 \pm 2.$$

There is thus no locus, but a tendency towards a value more or less constant in this range of pressure. This mean value of Y is 6.4 volts per cm.

17. The values of the ordinary Y 's in Table I. are in agreement with those given in my first paper (Phil. Mag., April 1908), although the latter were obtained with a constant current of 2.5 milliamperes. If the two discharge-tubes had been equal in diameter, having regard to the correction inferred above (1.6 *c*), we should expect Y in Table I. to be 3.4 volts per cm. greater than the corresponding value of the first paper, and not equal to it. But the present discharge-tube was 2.8 cm. in diameter as against the 2.4 of the first discharge-tube, so that the effect of the increased diameter appears approximately to balance the effect of the diminished currents on the electric force. There are no data for deducing the effect of the diameter of the tube on Y in oxygen; but if it is about the same as in nitrogen, the difference between the diameters of the two tubes would produce just about the difference in corresponding Y 's necessary to balance the 3 or 4 volts per cm. attributable to the difference of current. (See Herz's figures, *loc. cit.*)

Oxygen Discharges contrasted with Hydrogen Discharges.

18. In order to illustrate the anomalies of oxygen in this range of pressure by contrast with the behaviour of an ordinary gas, a series of determinations of the electric force in positive columns of hydrogen were made by the same

method and in the same apparatus and over the same range of pressure. The results are given in Table II.

TABLE II.

Hydrogen (p , Y , C as in Table I.).

p .	Y .	C .	p .	Y .	C .
1.35	26.7	.364	.66	14.5	.466
1.14	23.2	.215	.58	16.0	.121
1.14	20.7	.42	.51	14.5	.143
.85	19	.238	.29	11.1	.072
.82	17.3	.458	.28	11.6	.095
	18.8	.255	.24	11.9	.057
.66	16.3	.258			

Here $Y = 13p + 8.4$, except for the currents greater than .4.

If we omit the Y 's of the three currents greater than .4 (which, in view of what has been said above, will have electric forces sensibly less than would correspond to the mean of the other currents), the table, with the exception of one value of Y ($p = .29$), is represented by the equation

$$Y = 13p + 8.4,$$

within an error of 4 per cent.; which is thus the equation for currents adjacent to .2 milliampere for the range of pressure .24 to 1.35 mm.

If this line is drawn on fig. 4 it passes across the curve at a smaller slope, dY/dp , to the axis of pressure than that of the curve drawn in that figure. Nor is there any suggestion of discontinuity or arrest about it, though the values of Y corresponding to the same pressure are, up to the pressure .8, of very similar magnitude.

The big increase of electric force in the positive column per unit increase of pressure (current constant) is (as observed above, section 15) a characteristic of the ordinary discharges in oxygen at pressures where transition of current from ordinary to extraordinary takes place. In my first paper I gave the equation

$$Y = 25.6p + .9$$

for the constant current 2.5 m.a. and for pressures between .5 and .8 mm. in the tube of 2.4 mm. diameter. In this case the gradient dY/dp is 25.6, and the gradient of the curve of

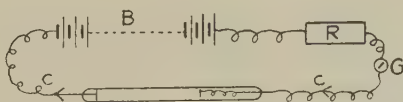
fig. 4 is, though less, of similar magnitude. The result of this fact is that small errors in the determination of the pressure may introduce serious ones into the values of Y . For instance, an error of .05 mm. would introduce an error of more than 1 volt per cm. in Y . This is to be borne in mind in estimating errors of observation, especially when it is necessary to compare values of Y determined with different McLeod gauges, the constants of which involve errors of determination, which might jointly produce discrepancies exceeding .05 mm. in the determinations of the same pressure.

Anomalies of Oxygen further illustrated.

19. The simplest way of illustrating the anomalies of oxygen and the sharp discontinuities that appear in the positive columns when the pressure is near the value .7 mm., is perhaps to plot the voltage-difference of the electrodes against the pressure when the latter alone is made to vary in an otherwise constant circuit of which the discharge-tube is part.

If the circuit consists simply of a constant battery B , a constant resistance R , a galvanometer G , and the discharge-tube T with its electrodes a fixed distance, D , apart as in fig. 5; then, if D is great enough to permit an adequate

Fig. 5.



positive column, the current C will undergo a sharp discontinuity at a certain (somewhat fluid) critical pressure in the neighbourhood of .7 mm.

Now the current is connected with the electrode potential difference by the linear equation,

$$X = B - CR,$$

so that the pressure-current curve is the orthogonal projection of the p - X curve. In particular, if R is a megohm and C is measured in microamperes and the battery is 1000 volts, the curves p - C , p - X are symmetrical with respect to the line parallel to the axis of p and distant 500 from it. One curve is the optical image of the other in this line. Such was roughly the state of things during the

experiments recorded in Table III., D being 19·7. Hence it is sufficient to draw the p -X curve for the purpose of illustration: the p -C curve looks practically the same but inverted. The exact details are given at the head of the table.

TABLE III.

Showing the variation of the voltage-difference X of the electrodes, and also of the electric current, C m.a., as the pressure varies up to 1·09 mm., with a constant circuit. Battery 1014 volts, and distance between electrodes 19·7 cm. Total ohmic resistance of circuit, galvanometer included, ·923 megohm.

p .	X.	C.	p .	X.	C.
1·09	498	·557	·66	524	·550
·89	502	·555	·65	606	·442
·79	510	·544	·60	602	·447
·66	622	·425	·54	584	·467
·75	498	·557	·50	576	·475
·71	504	·550	·40	560	·492
·68	504	·550	·38	560	·492
·67	504	·550	·32	552	·500
·66	504	·550	·27	551	·502

20. That the discontinuities exhibited in Table III. are due to the positive column is proved by Table IV., which applies to a fixed circuit as before (illustrated in fig. 5), with the difference that the influence of the positive column was practically removed by fixing the electrodes at the distance 7·9 cm. At the pressure ·29 the positive column was observed to begin 8 cm. away from the cathode. (Here the electric force was 9·2 volts per cm.) Hence the positive column in the case of all the experiments recorded in Table IV. was very short, and its effect on the discharge so slight as to obliterate the discontinuities which make their appearance with longer positive columns.

21. If the voltage-differences of the electrodes, X, in Table III. are plotted against the pressures, the greater values of X, namely those of the ordinary currents, which we call X_0 (section 24), determine a curve. This is shown very clearly in fig. 6, where the little crosses (or rather, their centres) are the points whose coordinates are corresponding

TABLE IV.

Showing the substantial constancy of the voltage-difference X of the electrodes, and also of the current C (m.a.), as the pressure p varies up to 1.12 mm., with a fixed circuit and little or no positive column. Battery 946 volts, $D=7.9$ cm. Total ohmic resistance of circuit .923 megohms.

p .	X .	C .	p .	X .	C .
1.12	446	.54	.49	420	.57
1.0	433	.555	.44	426	.56
.75	426	.563	.4	431	.56
.67	418	.575	.37	433	.555
.6	413	.577	.34	436	.552
.54	417	.575	.31	436	.55
.5	420	.57	.284.....	436	.55

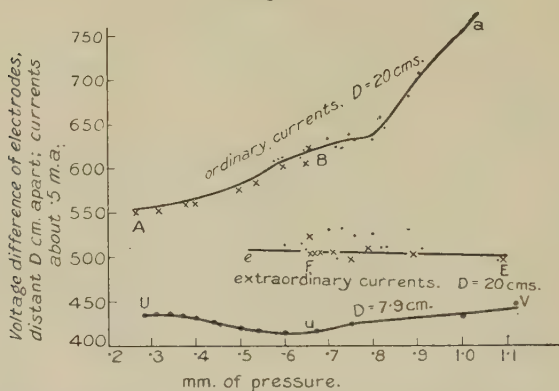
values of p and X in Table III. These apply to discharges in which the distance D between the electrodes is 19.7 cm., and those between A and B clearly determine a locus. The curve AB has been drawn slightly above that locus, and is the corresponding locus for $D=20$ cm. (The necessary correction is scarcely perceptible, being an addition to the ordinate X at any pressure of .3 Y , where Y is as usual the electric force in the positive column of the discharge and is given by the curve in fig. 4.) It will be shown below that the whole curve ABa is definitely determined by many other observations in addition to those of Table III., as the mean locus of the points p, X_0 when $D=20$ cm., for pressures up to about 1 mm., and currents of similar magnitude to .5 m.a., for which X_0 is practically independent of the current. (See section 27.)

The other values of X in Table III., namely the smaller ones which apply to extraordinary discharges, determine (with the exception of one) the straight line FE in fig. 6. But other determinations of X during the passage of extraordinary currents are by no means equally accordant to this result; for, as already noticed in sections 4 and 16, such currents are, unlike ordinary discharges, peculiarly susceptible to certain effects producible by the passage of electricity.

Table IV. similarly determines, and with precision, the curve UuV , which practically contains all the points plotted

on fig. 6 to represent the observations of that table. This curve will be discussed later.

Fig. 6.



22. The results so far described were obtained with self-determined discharges, which appeared as ordinary or extraordinary currents according to the pressure or magnitude. The following is an account of alternative currents through oxygen obtained without varying the pressure or the circuit.

Alternative Currents in a Discharge-tube of Oxygen in a given Circuit.

It is simplest to start with a detailed description of a selection of the experiments carried out in the manner described in sections 10 and 11 above with the arrangements illustrated in fig. 3. The notation and abbreviations used are given in section 24.

(i.) The ring of tinfoil, S, 3 cm. broad, fitting the discharge-tube with its edges at the distance 3 and 6 cm. from the cathode, the anode being 19.7 cm. from the cathode, and the pressure .84 mm., it was found that, when S was connected with the anode, the current was .47 m.a., which persisted when S was insulated, but changed at once to .33 m.a. on connecting S to the cathode, and so remained on insulating S. The change in E.P.D. (potential difference of electrodes) was from 555 to 683 volts.

(ii.) At the same pressure .84 mm. and the same distance, 19.7 cm., between the electrodes, but with the edges of S 2 and 5 cm. from the cathode, the current changed in the manner described in (i.) from 1.21 m.a. (E.P.D. 551 volts)

to $\cdot 965$ m.a. (E.P.D. 641), and from $\cdot 47$ m.a. (E.P.E. 558) to $\cdot 331$ m.a. (E.P.D. 687), and from $\cdot 442$ (E.P.D. 584) to $\cdot 331$ m.a. (E.P.D. 687).

The positive column was observed to begin 7 cm. from the cathode when the current 1.21 m.a. was passing, and 8 cm. from it during the discharge $\cdot 965$ m.a.

Further, the alternative currents 1.21 and $\cdot 965$ m.a. were easily made to alternate backwards and forwards by connecting the strip S to anode or cathode respectively (after which S could be insulated without affecting the current). But the smaller currents were not easily reversible. Finally the gas tended to lose this reversibility. (It is natural to attribute this to the loss of purity in the oxygen through the generation of ozone, as suggested by the slight observed decrease of pressure.)

(iii.) The copper ring, mentioned above, S (fig. 3), now replaced the tinfoil ring, just embracing the end of the positive column. With $D=21.8$ cm., $B=990$ volts, $p=\cdot 76$ mm., the current was made to alternate between 1.186 and $\cdot 883$ m.a., the P.D. of electrodes being 557 and 668 volts, and q (distance of foot of positive column from cathode) 7 and 8 respectively.

The electric forces in the two positive columns were found (section 12) by placing the electrodes 11.6 cm. apart and determining the reduction in the battery required to give the same extraordinary current 1.186 m.a., and again the reduction required to give the same ordinary current $\cdot 883$. These reductions were found to be 87 and 190 volts respectively, giving as the respective forces 8.5 and 18.6 volts per cm. To check these results the electrodes were placed 16.8 cm. apart, whereupon the batteries required to reproduce the same currents proved to be 939 and 900. These results show that the ordinary force is fairly accurately determined (within 3 or 4 per cent.), but that the extraordinary force is subject to much larger variations, being probably within 10 per cent. of the value 7.7 volts per cm. (See section 5 above.)

At the end of these experiments the pressure had fallen to $\cdot 74$, so that there may have been 5 per cent. of ozone in the gas during the last mentioned determinations.

It should be added that when the electrodes were only 7.7 cm. apart no alternative currents were obtained. This confirms what has been already established, that alternative currents in the same circuit in oxygen is a phenomenon of the positive column, practically at least.

(iv.) $p=1.04$ mm., $D=19.7$, distance of S from cathode = 7 cm. Alternative currents observed were .552, .248 ; .524, .271 ; .530, .226 : corresponding E.P.D.'s, 488, 770 ; 515, 750 ; 510, 791.

23. After these and a few other experiments, the apparatus was accidentally broken at the anode end. It was very ably repaired by Messrs. Townsend & Mercer's glass-blowers, and was reconstructed. A new cathode was inserted, 2.75 cm. in diameter, closely fitting the tube, as stated above. The following are details of some specimen observations.

(v.) $D=21.6$, $p=.61$ mm. The current was made to alternate between 1.075 m.a. ($X=592$ volts) and .91 ($X=654$) ; between 1.048 ($X=602$) and .885 ($X=667$) ; and eventually only the ordinary .91 m.a. was obtained.

(vi.) $D=21.6$. A little more oxygen was introduced bringing p up to .82, when the current was made to alternate between 1.02 m.a. and .745, the corresponding E.P.D.'s being 580 and 680 volts. This alternation was frequently produced backwards and forwards. But whereas the ordinary current .745 was stable and repeatable, the extraordinary varied, assuming the values .965, .91, etc., with E.P.D.'s 600, 620, etc.

(vii.) New oxygen. $p=1.03$ mm., $D=21.5$ cm., $B=1007$ volts. No transition here from the extraordinary current 1.38 m.a. ($X=503$). But the ordinary current .44 appeared and slowly crept up to the extraordinary .55, and there remained steady, X changing from 602 to 501 volts. This behaviour suggested that the gas was near the limit of the state which permits alternative currents of this magnitude to pass. These observations have not been included in Table V., since the gradual nature of the change throws doubt on the value of the ordinary current. In all the other cases the change was instantaneous.

The pressure was now reduced to .84, and D was 20.9. No alternations with the extraordinary current 1.23 m.a. ($X=559$), but alternations easily obtained between .66 and .44 (E.P.D.'s 560 and 710) ; and (with change of resistance in circuit) between .76 and .59 (E.P.D.'s 573 and 688) ; and (another change of resistance) between .746 and .564 (E.P.D.'s 583 and 686). Further, with the same specimen of gas and with D and p the same, and the circuit constant, the current was made to pass through the following alternations : .664, .442, .635, .442, .63 m.a., and the E.P.D.'s through the values 561, 710, 580, 710, 598 volts. The middle point of S was 6.5 cm. from the cathode.

Subsequently the current went through many alternations between .608 and .442 (E.P.D.'s 598 and 710), the distances of the positive columns from the cathode being 5 and 6 cm. in the extraordinary and ordinary currents respectively. And after many discharges the currents become .59 and .442 (X's 610 and 710).

These details are given to illustrate more clearly the striking constancy of the ordinary current, as contrasted with the steady diminution of the extraordinary. Thus, while the electrodes have maintained the constant value of 710 volts in the case of the ordinary currents of this long series of alternations, the potential difference of the electrodes during the passage of the extraordinary currents has undergone a steady increase from 560 to 610 volts, a total increase of 9 per cent. in X_e , involving an increase of 30 per cent. in the electric force in the positive column. (See sections 34 ff.) This throws light upon the great discrepancies observable in the determination of the electric forces in the extraordinary positive columns.

During this series of discharges the pressure fell from .845 to .82 mm., that is 3 per cent. If this was due to the formation of ozone, there would have been nearly 7 per cent. of ozone present at the end.

We may conclude from these detailed results that while both kinds of currents are perfectly determinate and precise, the ordinary are constant and repeatable, and the extraordinary, on the other hand, depend to a considerable extent on the past electrical history of the gas; for the currents which pass through the gas have an accumulative effect on it, probably due to the production of ozone.

24. The foregoing accounts will sufficiently describe in detail the nature of this peculiar property of oxygen and the method I used to investigate it. Many other similar experiments were made, giving similar results, most of which are collected in Table V.

Notation employed in Table V. and throughout this paper.

Each line in Table V. applies to a fixed circuit as illustrated in fig. 3, permitting alternative steady currents C_o , C_e through the discharge-tube.

p is the pressure in mm. of mercury,

D the distance in cm. between the electrodes,

C_0, C_e are the ordinary and extraordinary currents respectively in milliamperes,

X_0, X_e the voltage-difference of electrodes during the passage of C_0, C_e ,

Y_0, Y_e the electric force in volts per cm. in the positive columns of C_0, C_e ,

q_0, q_e the distance in cm. from the cathode of the foot (nearest point) of the positive column of C_0, C_e , so that $D - q_0, D - q_e$, are the lengths in cm. of those positive columns.

(The above notation is also used without the suffixes, when the nature of the current is not specified.)

B, R are the voltage of the battery, and the total ohmic resistance, of the circuit, respectively.

m.a. denotes as usual milliampere, and

E.P.D. denotes electrodal potential difference (X).

The values of B, R are not given in Table V., because they are incidental features of the phenomenon, and also because they are easily obtained from the equations

$$B = X_0 + C_0 R = X_e + C_e R, \quad . \quad . \quad . \quad (1)$$

whence $R = (X_0 - X_e)/(C_e - C_0)$.

For instance, taking the numbers for the pressure $\cdot 564$ in Table V., we get $R = \cdot 374$ megohm, $B = 956$ volts. The recorded values were $\cdot 365$ megohm, 948 volts, so that even when C_0 and C_e differ by a comparatively small fraction of their values, B and R are recoverable, if required, within a small percentage.

Remarks about Table V.

25. The range of pressure in this table is that within which the phenomenon of alternative currents was observed. No doubt the range might be extended by a more effective method of producing the transition from extraordinary to ordinary current at pressures greater than $1\cdot 04$, and from ordinary to extraordinary current at pressures less than $\cdot 54$ mm.: *e. g.* by using higher or lower voltages than those of anode or cathode to charge the ring S with.

The distance D , separating the electrodes, is, in all but a few cases recorded in Table V., about 20 or more centimetres, but otherwise arbitrary; such distances being great enough for the purpose in view, but not too great for the battery to maintain steady currents in the discharge-tube at the pressures recorded.

TABLE V.

p .	D.	C_0 .	X_0 .	Y_0 .	q_0 .	C_e .	X_e .	Y_e .	q_e .
1.04	19.7	.248	770552	488		
1.04	19.7	.27	750524	515		
1.04	19.7	.226	79053	510		
.89	20.8	.86	676	...	6	1.15	569		
.88	21.2	.441	68558	552		
.84	20.9	.44	71066	560		
.84	19.7	.331	68747	558		
.84	20.9	.59	68876	573		
.82	21.6	.745	680	...	6.5	1.02	580		
.81	19.5	.408	625497	540		
.76	21.8	.883	668	18.6	8	1.19	557	8.5	7
.74	19.7	.416	620496	545		
.73	21.2	.855	656	1.08	576		
.73	21.2	.662	66081	595		
.72	21.4	.36	67452	524		
.7	21	.359	669	...	7	.496	540	...	6
.65	21.3	.386	651	20.653	519		
.61	21.6	.91	654	1.07	592		
.6	19.7	.82	588	18.3	...	1.06	501	11.8	
.6	23.1	.83	649	18.3	...	1.12	541	11.8	
.6	23.7	.483	681	18.9705	532		
.59	23.8	.354	680494	550		
.59	20.5	.386	610496	508		
.59	17.1	.398	558450	507		
.58	24.2	.328	685	17.546	563		
.58	17.7	.433	568496	510		
.565.....	24.4	.336	687	17.2485	547		
.564.....	22	.91	616	14.6	...	1.1	545	9.3	
.56	18.5	.494	564	17.5585	502	7.6	
.56	24.8	.48	675	17.6663	550		
.55	21.5	.99	630	1.19	555		
.54	21.4	1.1	604	...	8	1.3	533	...	7
.54	21.4	.6	601	...	8	.72	521	...	7

The values of X_0 , X_e were in most cases thus determined:—Before passing the current through the discharge-tube T (fig. 3), T was short-circuited by connecting the right and left mercury cups at M, and the current read on the

galvanometer. Let this reading be K . If now on insulating these cups the current C_0 passes through the discharge-tube (read on the same galvanometer), X_0 is immediately given by $B(K - C_0)/K$ volts, whatever the constant of the galvanometer. Similarly for X_e .

In the case of the galvanometer thus used, the errors of observation would not have exceeded in general one or two per cent.

The values of Y_0 , Y_e in Table V. were determined by the method explained in section 12. But in reproducing, *e. g.* the current C_0 in the discharge-tube, when B and D are suitably reduced, C_e will be altered; for the ratio of C_0 to C_e diminishes with the length of the positive column. In applying this method, if no transition of current is producible with reduced B and D , it is at least necessary to know whether the current that appears is the ordinary one or the extraordinary.

As for q_0 , q_e , the discharge is often so faintly luminous that it is difficult to be sure of their values within .5 cm. Still, the positive columns of both ordinary and extraordinary discharges look perfectly regular and determinate. And when the transition is effected backwards and forwards, the extraordinary positive column shrinks back about 1 cm. and distinctly gains in brightness, and then moves forward again as it resumes its paler shade. (See section 30 below.)

26. The currents C_0 , C_e change freely when the ohmic resistance R is varied. The ratio C_e/C_0 , always greater than unity, is not a simple one. It diminishes as the positive columns are shortened, that is as the anode is brought nearer the cathode, and tends towards unity when the positive columns are thus made to disappear. Moreover, as shown above (section 23, vii.), C_0 remains constant after many discharges have passed through the gas, whereas C_e undergoes a steady increase, so that the ratio tends to increase, when the circuit remains unchanged, through the electrification of the oxygen. With D about 20 cm., the pressure ranging from .5 to 1 mm., and currents not exceeding a milliampere, the ratio of C_e to C_0 should range from about 1.2 to 1.5.

27. The E.P.D., X_0 , during the ordinary discharges, is nearly independent of the current C_0 , when the latter's range of variations is that of Table V. At least, X_0 only varies by a small percentage. This is shown by Table V. It is also accordant with the results obtained and discussed

in section 14 above, which show that Y_0 is only to a limited extent dependent on currents of our order of magnitude. For X_0 is roughly equal to Y_0 , multiplied by the length of the positive column, plus the constant cathode fall of potential; so that percentage variations in Y_0 produce in our discharges less than half such variations in X_0 , since the fall of potential down the positive column, $(D - q_0)Y_0$, was in every case less than the cathode fall, and Y_0 can only be affected to the extent of 3 per cent. by the variation of current shown in Table V. Hence any considerable percentage discrepancies in the values of X_0 in Table V. must be attributed to other causes.

The same might be true of X_e and C_e , if it were not for their tendency to undergo accumulative changes under the action of the discharge.

Some General Details.

28. During the experiments represented in Table V., it was verified that when once the discharge had started or had been transformed from the ordinary to the extraordinary or *vice versa*, it was not affected either by insulating the ring S from anode or cathode, or by earthing it. Hence the ring, though useful for starting the discharge or transforming it, does not disturb the discharge appreciably.

A curious effect may be noticed. When the distance between the electrodes was too great for the discharge to start with the battery B (about 1000 volts), at a certain pressure (*e.g.* 1.04 mm.), the discharge was easily started by connecting S to the anode. But after being stopped it would not restart in the same way till this connexion had been broken and the ring S earthed or connected to the cathode. This effect was doubtless due to electrons adhering to the inner surface of the discharge-tube in the neighbourhood of S, so long as it was at a positive potential, and so neutralizing to some extent the electric force set up in the gas between the cathode and the ring.

Position of the Ring S.

29. It was observed that the ring had to be near the foot of the positive column to effect the alternation of current. If S is one or two cm. up the column, only the ordinary current would appear on connecting S to the anode. On the other hand, if S was one or two cm. nearer the cathode,

the extraordinary started on connecting S to the cathode but then stopped.

Generally speaking, S was best placed just outside the positive column of the (longer) extraordinary discharge, so that the foot of the column of the ordinary discharge fell about a cm. short of it.

Positive Columns of Alternative Currents contrasted.

30. When the transition from the ordinary discharge to the extraordinary takes place, the current increases in magnitude, and the positive column increases about a cm. in length and loses in brightness. This latter effect is paradoxical, for the general effect of increasing the current through a gas is to increase the brightness of the positive column. The explanation must be that the intensity of the brightness of the positive column depends not only on the current-strength but also on the electric force within the positive column, and that the great reduction of this force, when the transition in question takes place, more than balances the increase of current.

In the case of ordinary positive columns, I have occasionally observed striæ of a type peculiar to oxygen. They are thin luminous disks and not curved. They are a very pretty phenomenon. In my first paper (Phil. Mag. April 1908, p. 565) I mentioned some so close together that 10 were within 1·8 cm. These appeared at ·8 mm. about, with the zinc electrodes. On the present occasion, at the pressure ·27 mm., I noticed similar band-like striæ about 2 mm. thick and about 8 mm. apart in considerably used oxygen, the current being ·247 m.a.; and also at the pressure ·55, current ·276 m.a., striæ much closer together, namely $3\frac{1}{2}$ to the cm. I have not observed striæ in the columns of extraordinary discharges.

Transition of Current Effected by touching the Discharge-tube.

31. In earlier experiments the alternative current was produced by simply touching the discharge-tube during the passage of the extraordinary current. About half of these observations are given in Table VI., the rest of them being omitted because they agree so closely as to be practically repetitions. In every case the distance between the electrodes was 20 cm., the battery was 990 volts and the total ohmic resistance, including that of the galvanometer (36,240 ohms), was ·911 megohm.

TABLE VI.

D=20 cm, B=991 volts, R=.911 megohm.

<i>p.</i>	$C_e \longrightarrow C_0$	$X_e \longrightarrow X_0$		
1.4463	...	568	
1.25535	...	501	
1.08543	...	531	
.91524	.309	510	706
.885	.334	531	683
.83522	.373	511	647
.82524	.364	510	656
.8505	.389	527	633
.76508	.389	524	633
.75539	.386	500	639
.735	.4	532	623
.72539	.401	499	624
.7502	.392	531	632
.65529	.408	507	618
.64521	.416	515	611 *
.6522	.417	514	611
.59418	...	610
.58420	...	608

Transition of current effected by touching the discharge-tube.

* This transition of extraordinary to ordinary current was spontaneous.

Other transitions of greater currents were effected by keeping a finger on the discharge-tube, but the transition was reversed on removing the finger. Thus at the pressure .8 mm. the current (C_e) 1.37 m.a. changed into .99 (C_0), the E.P.D. (X_e) 492 changing into (X_0) 628; and similar effects were obtained between .7 and .91 mm. These observations illustrate the rule stated in section 14, that the greater the current, the lower the pressure at which it appears spontaneously as an ordinary discharge.

Again, between .7 and .81 mm., both currents showed a tendency to diminish slowly. In this region of pressure the discharge readily undergoes transition. In such cases the mean value of the observed currents is given in Table VI., which, however, only differ from the extreme values by about 2.5 per cent.

General Results.

32. The uppermost curve of fig. 6 is the mean curve determined by all the values of X_0 corresponding to pressures between .25 and 1.04 mm. for the electrode distance 20 cm., the current being adjacent to .5 m.a. but otherwise arbitrary; for with this condition we have seen that the E.P.D. is practically independent of the current. These values are obtained from Tables III., V. and VI. Table III. determines the portion AB of the curve accurately as fully explained in section 21. Table VI., which applies to $D=20$ cm., determines the points on fig. 6 which are indicated by dots; and of these, those which belong to ordinary discharges lie close to the upper part of AB or to Ba which is a continuation of AB.

In the case of Table V., it is necessary to decrease (or increase) the value of X_0 , corresponding to any electrode distance D by $(D-20)Y_0$, in order to make it apply to $D=20$ at the same pressure; where Y_0 is the electric force in the positive column of the current in question. For this purpose of adjustment, Y_0 may be taken from Table V., or from the curve of fig. 4, or from the formula $Y_0=(X-413)/(D-q_0)$, when p exceeds .65 mm. (See section 37 below.)

The values of X_0 thus contributed by Table V. (about thirty), when plotted against their pressures, determine points which all lie close to the curve, or within 3 per cent. of those values from the curve, except about two which differ by five per cent. from the ordinates of the curve. Hence we may say that the curve is the locus of the points p, X_0 given by all our observations within the errors of those observations.

These results prove that the ordinary currents are determinate features of oxygen, and are not dependent on the means used to produce them. Nor are they affected, at least to any great extent, by the past electrification of the gas.

33. On the other hand, when the extraordinary currents are passing, the E.P.D.'s are by no means so coordinate. This is to be expected from the discordant values of the electric force in the positive columns of such currents, shown in Table I. and fig. 4. The gas seems to be modified by discharges passed through it, so that the current undergoes a gradual decrease and the E.P.D. a gradual increase when a series of discharges are passed through the gas in a fixed circuit. (Section 23, vii.) Now Table III. determines a number of points in fig. 6 whose coordinates are p, X_0 , and all of these except one lie close to

the line FE. These points are indicated by the small crosses. In the same way Table VI. gives a number of points shown by the dots, and these approximate closely to FE or its continuation eF , or else lie above the line eFE ; and the same thing is true of the large number of points contributed by Table V. after correcting the values of X_e so that they apply to $D=20$ cm. (which correction does not exceed about a volt per mm. increase of D). Hence we may conclude that the line eFE is very nearly the locus of the points whose coordinates are p , X_e , when the electrodes are 20 cm. apart and extraordinary currents of the order .5 milliampere are passing through oxygen, undisturbed by previous electrification; for the effect of such disturbance is to bring those points above that line.

It follows that the ordinary and extraordinary currents in a given circuit are two stable forms of discharge which oxygen in a conducting state may assume, the one form being practically unaffected by, and the other modified in an accumulative manner by, previous discharges through the gas.

Deduction of the Electric Forces in Alternative Currents.

34. From fig. 6 we can deduce approximately the mean normal value of the electric force in the positive columns of the alternative discharges in fixed circuits, studied in this paper (additional to the values of Table I.).

For the value of Y_0 can be derived approximately from the value of X_0 , if q_0 is known, by means of the equation

$$Y_0 = (X_0 - F)/(D - q_0), \quad . \quad . \quad . \quad (2)$$

where F is the value of the E.P.D. when $D=q_0$ and the current is the same, so that the positive column has just disappeared. And if the current is only roughly the same, that is of the same order, equation (2) will be still nearly correct*, X_0 being only to a limited extent dependent on the current. (Section 27.)

Now F is nearly constant in oxygen with our range of pressure and current. This is shown in Table IV., and by the curve UuV in fig. 5, which represents that table graphically, applying to discharges between electrodes 7.9 cm. apart. For q_0 is about 8 cm. for pressures below .65 mm.,

* Where there are striæ in the positive column, equation (2) would give the average value of Y_0 , or, *mutatis mutandis*, of Y_e . But in oxygen striæ seldom appear (see section 30), at least at our pressures, so that the force within the positive column of both ordinary and extraordinary currents may be assumed to be constant.

and decreases to 6 cm. as the pressure rises from $\cdot 65$ to 1 mm.

35. The lowest E.P.D. in the curve alluded to in fig. 6 is 413 volts *, namely when $p = \cdot 6$ to $\cdot 65$ mm. When p is less than this, the E.P.D. slightly increases, probably because the cathode fall of potential is becoming more than the "normal cathode fall," the current being more than sufficient to cover the cathode. And as p increasingly exceeds $\cdot 6$ mm., a portion of positive column makes its appearance, increasing up to 3 cm.; for these discharges, being self-determined, would have been at such pressures extraordinary currents (see Table III.), and q_e is about 5 cm. when $p = 1$ mm. (Table V.).

36. From these considerations it follows that for pressures below $\cdot 65$ mm. (whereabouts the abrupt change tends to take place, from ordinary to extraordinary current) the electric force in the ordinary positive column is equal to the difference of the ordinates of the upper and lower curves, AB, Uu , of fig. 6 divided by the difference between the electrode distances (20, 7.9 cm.) which are constant for these curves, that is by 12.1 cm. In fact, the values of F in equation (2) are practically the same as those of the ordinates of Uu , and q_0 is nearly 7.9 cm. for pressures below $\cdot 65$ mm.

Again, when the pressure exceeds $\cdot 65$ mm., the difference of ordinates, at any pressure, of the (straight) curve FE ($D = 20$) and the lower curve UV ($D = 7.9$) divided by 12.1 gives the electric force in the extraordinary positive column at that pressure; for both curves now refer to extraordinary currents.

37. The electric force in the positive column of *ordinary* currents when the pressure is above $\cdot 65$ mm. cannot be deduced correctly by the same method, which would introduce a considerable percentage error (up to 10 per cent. at

* That the voltage 413 is the value of X_0 when $D = q_0$ and the cathode fall is *normal*, or nearly normal, appears from the following considerations. With platinum electrodes the normal fall in oxygen is 369 (Capstick), and the same figure may be presumed with our gold electrodes. Now the rise of potential between the cathode and the foot of the positive column, in the case of hydrogen and nitrogen, is the cathode fall plus a voltage less than $\frac{1}{2}xY$, where x is the distance between the negative end of the Faraday dark space and the foot (nearest point) of the positive column (See the diagrams in Sir J. J. Thomson's 'Conduction of Electricity through Gases,' 1903, c. xv.) In our case with $p = \cdot 6$ mm., and $Y = 18$ volts/cm., x should be less than 6 cm., if we are guided by the behaviour of those other gases. Therefore F should be less than 423. Hence the figure 413 should apply to a discharge with a practically *normal* cathode fall, in order to satisfy the above inequality.

1 mm. pressure) in excess of Y_0 . For the ordinate to the curve Ba ($D=20$) at a pressure greater than .65 applies to an ordinary current, and the ordinate at the same pressure to the lower curve ($D=7.9$) applies to an extraordinary current with a short length of positive column of low electric force. Hence we have to use the formula (2), where $F=413$, and $D=20$, although the values of q_0 are only roughly known from Table V. These values are 7, 7, 6 cm. for the pressures .7, .8, .9 mm., involving an error that can scarcely exceed .5 cm. Thus we derive from equation (2) the values of Y_0 , 16.3, 17.2, 20.5 volts/cm., for the pressures .7, .8, .9; in which the percentage errors arising from the assumed values of q_0 should be less than 4 per cent. Further, since q_0 must be assumed to lie between 6 and 5.5, when $p=1$ mm., we obtain for Y_0 ($p=1$) the value 23.6.

38. The approximations thus obtained to the values of Y_0 , and Y_e , are collected in Table VII.; which also contains, for the sake of reference, the mean values of X_0 , and X_e for $D=20$, and the values of X for $D=7.9$ cm. The latter are derived from the ordinates of the curve UuV , which applies to neutral discharges, neither ordinary nor extraordinary, (for with no positive column no such distinction can be made), except when the pressure exceeds about .65 mm., when the ordinates are X_e . But this distinction is not made in the table.

TABLE VII.
(For notation see section 24.)
Currents of order .5 m.a.

p .	$D=20$ cm.		$D=7.9$.	Y_0 .	Y_e .
	X_0 .	X_e .	X .		
.3	555	...	436	9.8	
.4	565	...	431	11.1	
.5	580	...	420	13.2	
.54	590	509	417	14.3	
.6	608	508	413	16.1	
.65	617	506	415	16.7	7.5
.7	625	504	419	17.0	7.0
.75	633	504	424	17.3	6.6
.8	637	503	427	17.4	6.3
.9	700	502	432	20.5	5.8
1.0	750	501	437	23.6	5.3
1.1	500	440	...	5.0

The X_0 's, for $D=20$ cm. in Table VII., derived from the upper curve of fig. 6, are the mean results of so many observations that they ought not to be infected with the same percentage errors to which individual observations are liable in electrical experiments on gases at such low pressures; though the errors of observations on *ordinary* discharges are not normally, as we have seen, more than a few per cent.

The values of X_e are approximately the values of the E.P.D. of extraordinary discharges, also of order $\cdot 5$ m.a., through oxygen unaffected by previous electrification.

The values of Y_0 are in satisfactory agreement with Table I. and fig. 4, except for the discrepancy at the pressure $\cdot 6$ mm., where the latter gives 18 volts/cm. The value 16.1 of Table VII. agrees accurately with the run of the curve of fig. 4. But in section 15 reasons have been given for not discarding the value 18, and the discrepancy, 1.9 volts/cm., must remain unresolved.

As for the values of Y_e in Table VII., they agree fairly well with the lowest values of Y_e given in Table I. and fig. 4, which are presumably the values of Y_e in oxygen previous to electrification.

39. This general agreement of Table I., all derived from individual experiments described in section 12, with the results of Table VII., deduced from the joint data of so many other observations, shows once more that there are two definite modes of the passage of electricity through oxygen at pressures between a certain range (of which, as so far observed, $\cdot 8$ mm. is about the centre), and that the gas at such pressures can conduct electricity in the same circuit in one or other of these two modes, which the oxygen may adopt spontaneously or through control, provided that the alternative currents are of certain orders of magnitude.

Influence of a Mixture of Air on the Transition of Current.

40. A few experiments were made to see to what extent oxygen must be pure to permit alternative currents to pass in a given circuit in circumstances where they appear in pure oxygen. Oxygen was mixed with a considerable proportion of air, so that the mixture contained 88.4 per cent. of oxygen and 11.6 per cent. of nitrogen (and argon, etc.). Between the pressures $\cdot 81$ and $\cdot 52$ mm., $D=19.8$ cm., currents of extraordinary type and magnitude $\cdot 5$ or rather less, and of magnitude greater than 1 m.a., passed; but the only transition observed, and that on touching the tube, was at

the pressure .65, when .475 m.a. (C_e) changed to .386 (C_0), the corresponding change of E.P.D. being from 528 (X_e) to 611 volts (X_0). These alternatives are so similar to the numbers given in Table VI. at the same pressure, but with a slightly different circuit (battery and resistance), that we may conclude that the oxygen, even with such a large percentage of nitrogen, had not lost the peculiarity of alternative currents, but had lost the facility of exhibiting it.

No Change of Pressure observed during Transition of Currents.

41. It is natural to suppose that the two different modes of conducting electricity which oxygen possesses at certain pressures may be associated with two different molecular states which the gas might be made to alternate between at those pressures. A change from one such state to the other would be accompanied by a change of pressure, unless it consisted of a passing *pari passu* into ozone and monatomic oxygen, in which case the pressure would remain constant. In order to see whether any change of pressure, detectable by the McLeod gauge, arises with transition of current, the pressure was carefully read during an extraordinary discharge with current of order .5 m.a. at the pressure .83 mm., and again about thirty seconds later. The current was then switched without stopping it to the alternative ordinary form, and similar observations were made. The fall in each case was very small, namely of the order .0016 mm., such as is always to be expected with oxygen in such conditions, and contained in such a volume, which was nearly 600 c.c.

These results prove that no *local* change of pressure occurs during the discharge in the discharge-tube. For such a change would have produced a change of pressure in the oxygen in the bulb of the McLeod gauge (which belonged to the same volume with the discharge-tube), and so could not have escaped detection. But the results do not settle the question whether there may be produced by the discharge, at the moment of transition of the current, a general molecular change, with change of pressure, in the whole mass of the gas filling both discharge-tube and gauge. For in using the latter, the gas in its bulb was compressed to a pressure of 264 mm., at which it would have recovered the ordinary molecular condition of oxygen. Thus whether the latter is assumed to go with ordinary or extraordinary discharges, no change of pressure could be detected by the McLeod gauge. Nevertheless the negative result of these

observations of pressure during the discharges of both types makes it most improbable that any molecular change involving change of pressure takes place with transition of current.

42. The phenomena described in this paper are an extension of the effects of which I gave an account in *Phil. Mag.* April 1908, and summarized in section 2 above. In the latter paper I raised the question whether the electrical discontinuities at about $\cdot 8$ mm. were connected with the discontinuity in conforming to Boyle's law in oxygen at the pressure $\cdot 7$ mm., described by C. Bohr in *Wied. Ann.* vol. xxvii. p. 459 ff. (1886), and confirmed by other physicists, although Lord Rayleigh with the most careful investigation and with Bohr's result in his mind entirely failed to discover any such departure from Boyle's law in the neighbourhood of $\cdot 7$ (Phil. Trans. 1901, p. 205). The results established in the present paper, however, show that the abrupt changes of current are not discontinuities in the strict sense of the word, but sudden shifts from one to the other of two possible modes of conduction of electricity through the oxygen at certain pressures and with certain orders of current associated with those pressures. Both these modes are regular and continuous with continuity of pressure; but the one is constant and the other is liable to modification by the past treatment of the gas. If these *are* associated with different molecular states, one of those molecular states, that of the ordinary currents, might conform to Boyle's law consistently, but not necessarily the other.

In conclusion, I wish to express my obligations to Mr. E. P. Cardew, who helped me in the early part of this research and established the very suggestive fact that the transition from extraordinary current to ordinary could be effected by touching the discharge-tube.

All the experiments were made in the writer's private laboratory in Saham Toney Rectory, Norfolk. The battery used in this and other researches was practically covered by a grant from the Royal Society in 1911, made originally for an investigation connected with the positive column of oxygen, and I wish to express my thanks for it in this paper.

LXXXIII. *An Application of Diffraction Halos to Elasticity.*
 By JAS. P. ANDREWS, B.Sc., *East London College* *.

WHEN lycopodium is dusted on any polished plane surface, the image of a small light placed in front of it appears surrounded by circular coloured rings. On deforming the surface in any way, the rings change their shape, and some measure of the strain may thus be obtained. The following describes how Poisson's Ratio may be determined by this method.

The halos here obtained are formed in the same manner as those seen in a mirror with a silvered back, whose front surface is dusted with fine powder, and which have been fully described and explained by Stokes †. The illuminated particle sends secondary wavelets to the eye both directly and by way of the regularly reflecting surface, the retardation between these two routes determining the colour seen. It is at once clear that light of wave-length λ , and of a given order of interference, will issue from the surface at a particular angle, α_λ , with the normal at that point. Then if the surface bends and the normal be made to rotate, the angle at which the rays enter the eye must change and the halo be deformed.

A uniform rectangular brass plate P, one surface of which is polished and dusted with lycopodium, is bent by couples at its ends, and placed a few feet from a small light L_1 . An observer at E (fig. 1) can measure the diameters of the elliptical halos upon the superposed image of the screen S, which is seen by reflexion in the glass plate G. S is an opaque screen, pierced by two perpendicular rows of fine equidistant holes, illuminated by light L_2 . The distance of S from G may be arranged so that parallax between the images of S and L_1 is quite small.

The observer measures the lengths of the major and minor axes of one of the coloured bands, and then bends the plate a little more and repeats the measurement. Let x be the angle subtended at the eye by the diameter which is in the plane of bending, and y that subtended by the perpendicular diameter. On bending further, let these change to x' and y' . Then

$$\text{Poisson's Ratio } \sigma = \frac{\frac{1}{y'} - \frac{1}{y}}{\frac{1}{x} - \frac{1}{x'}}.$$

* Communicated by the Author.

† G. G. Stokes, *Math. and Phys. Papers*, vol. iii. p. 174.

For if OPQ is a portion of the surface (fig. 2), and x is the angle subtended by the diameter considered, let C be the

Fig. 1.

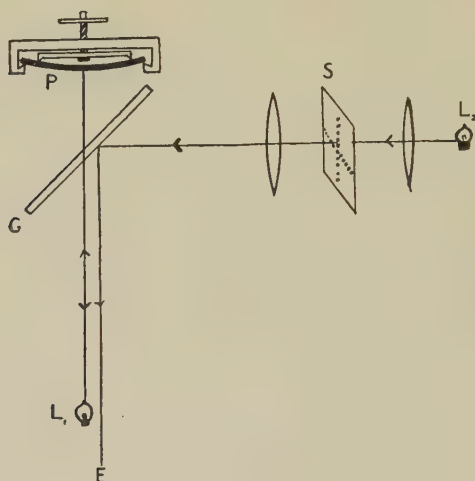
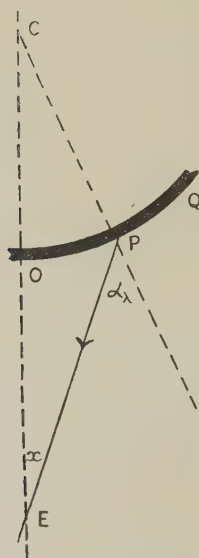


Fig. 2.



centre of curvature of the surface, whose radius of curvature is r , and let $OE = d$, the distance of the plate from the eye.

Angle EPQ = α_λ , and $\alpha_\lambda = x + \frac{OP}{r} = x + \frac{xd}{r}$ approximately;

hence $\frac{\alpha_\lambda}{x} = 1 + \frac{d}{r}$: similarly $\frac{\alpha_\lambda}{x'} = 1 + \frac{d}{r'}$.

Therefore $\alpha_\lambda \left(\frac{1}{x} - \frac{1}{x'} \right) = d \left(\frac{1}{r} - \frac{1}{r'} \right)$.

Similarly for a direction at right angles,

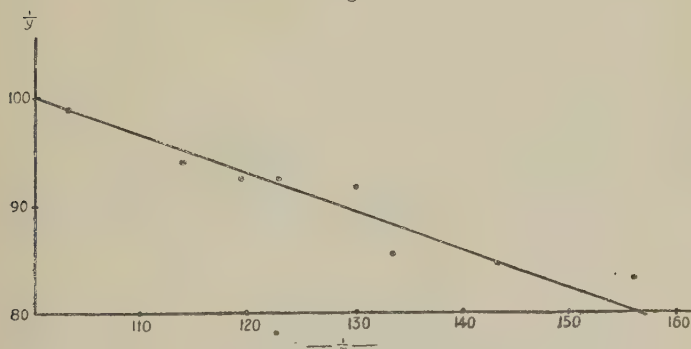
$$\alpha_\lambda \left(\frac{1}{y} - \frac{1}{y'} \right) = d \left(\frac{1}{R'} - \frac{1}{R} \right).$$

Now $r = \sigma R$ and $r' = \sigma R'$; so that finally

$$\frac{\frac{1}{y'} - \frac{1}{y}}{\frac{1}{x} - \frac{1}{x'}} = \sigma.$$

The halos are generally small and diffuse, and do not improve on bending the plate; great accuracy cannot therefore be attained. The graph below shows a series of results, $\frac{1}{y}$ being plotted against $\frac{1}{x}$.

Fig. 3.



The results of six series of this kind are as follows:—

$$\sigma = \cdot 40, \cdot 48, \cdot 37, \cdot 33, \cdot 37, \cdot 25;$$

mean value of $\sigma = \cdot 37$.

Although the method is capable of some improvement, it is presented rather as an interesting variant of the usual experiments with the diffraction halo.

LXXXIV. *The Striated Distribution of Space Charge.*
By B. M. CASSEN *.

SUMMARY.

IT is shown that, in the statistically steady state, striations will, in general, exist in an electric discharge, even when the rate of ionization is constant at all points along it. The case where one ion is much more mobile than that of the opposite sign is treated analytically. An exact solution of the equations expressing the electric potential as a function of the distance along the discharge is obtained in terms of elliptic functions. The formula, involving the complete elliptic integral for the real period of the potential, gives an exact expression for the distance between the striations as a function of physical quantities determining the state of the discharge. The condition that the rate of ionization in the discharge is constant along it does not prevent the application of the analysis to ordinary discharges, if account is taken of ionization by radiation as well as by collision. A practical form of the formula for the distance between the striations shows why that distance varies roughly as the inverse square root of the pressure, why the striations usually tend to become concave towards the anode, why the striations become closer together in a constriction in the tube, and why they are affected by small amounts of foreign gases; it also predicts a separation of the striations with increasing temperature.

IN general, for a discharge in the steady state, electrically and thermally, between two plane-parallel electrodes through a gas which is ionized into one type of positive ion and one type of negative ion in equilibrium, with respect to their rates of formation and recombination, the following relations hold :

$$\frac{d^2V}{dx^2} = 4\pi(\rho_2 - \rho_1), \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$I_1 = \rho_1 v_1, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$I_2 = \rho_2 v_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$I = I_1 + I_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$\rho_1 \rho_2 = \epsilon_1 \epsilon_2 \frac{q}{\alpha} + \frac{\epsilon_2}{\alpha} \frac{dI_1}{dx} = K, \quad . \quad . \quad . \quad (5)$$

* Communicated by Prof. S. Chapman, M.A., D.Sc., F.R.S.

where V is the potential in electrostatic units at a point x cm.
 from the cathode, relative to the cathode,
 ρ_1 is the density of positive electricity in electrostatic
 units per cm.³,
 ϵ_1 is the charge of the positive ion in electrostatic
 units,
 v_1 is the mean velocity of positive ions,
 I_1 is the current per cm.² carried by positive ions,
 $\rho_2, \epsilon_2, v_2, I_2$ have similar significance, but pertain to the
 negative ion,
 q is the number of ions produced in one cm.³ in one
 second,
 α is the recombination coefficient of the ions.

Equation (5) is simply the particular case, for the steady state, of the well-known equations forming the basis of the simple theory of ionized gases as given by J. J. Thomson *, and no remarks are necessary on the first four equations.

Considering $V, \rho_1, \rho_2, I_1, I_2, v_1$, and v_2 as functions of x , but I and K independent of x , in the steady state, there are five independent relations connecting these seven functions of x . It is necessary to have two more relations to determine these quantities completely as functions of x . Of course, the truth of (5) precludes those cases where the mean free paths of the ions are comparable with the distance between the electrodes, so that there is no simple relation connecting V with v_1 and v_2 as there is at extremely low pressures.

Attempts † have been made to develop the theory of the distribution of potential along a discharge by assuming that the ions have constant mobilities μ_1 and μ_2 respectively, giving as the two relations to complete the theory

$$\left. \begin{aligned} -v_1 &= \epsilon_1 \mu_1 \frac{dV}{dx} \\ v_2 &= \epsilon_2 \mu_2 \frac{dV}{dx} \end{aligned} \right\} \dots \dots \dots (6)$$

This procedure does not give very satisfactory results, which could, in fact, hardly be expected, in view of the fact that μ_1 and μ_2 are unknown functions of ρ_1, ρ_2, v_1 , and v_2 , and cannot be taken as constants with respect to these, especially to the first two. J. J. Thomson ‡ has more recently used

* See 'Conduction of Electricity through Gases.'

† See J. J. Thomson, *loc. cit.*

‡ Phil. Mag. xlii. p. 986 (1921).

relations based on the probability of an ion retaining a certain portion of its kinetic energy in the direction of the field, after impact. He does not assume that q is constant, and the way in which he assumes it to vary with the potential gradient and current density introduces a periodicity into the nature of the discharge. The assumption only takes into account part of the ionization. The principal other source of ionization is the radiation emitted by recombination of ions. This and other effects that have been studied in low voltage arcs evidently tend to smooth out the production of new ions, so that in most cases it would seem that the actual conditions in the positive column of a discharge or in a low voltage arc can be fairly approximated by assuming q independent of x . As will be seen in what follows, it is possible for striations to exist in a discharge even when this assumption is made, and in general they must always be present except in a particular case where the period of the striations becomes infinite.

When the positive ions, for example, have a negligible mobility in comparison with the negative ions, then v_1 can be assumed to be practically zero, and it is only necessary to obtain one valid relation to solve the equations. This case will be the only one fully treated in this paper. A final relation can be obtained from purely statistical considerations applied to the distribution of the positive ions in the field. Boltzmann's distribution law gives immediately for the region of the discharge under consideration

$$\rho_1 = \gamma e^{-\frac{\epsilon_1 V}{kT}}, \quad \dots \dots \dots (7)$$

where k is Boltzmann's constant, T the absolute temperature, and γ a constant. To evaluate γ , let V_M and V_m be the maximum and minimum potentials in the region under consideration, then in this region the average value of the charge density of positive electricity is

$$R_1 = \frac{1}{V_M - V_m} \int_{V_m}^{V_M} \rho_1 dV = \frac{\gamma kT}{\epsilon_1 (V_M - V_m)} \left[e^{-\frac{\epsilon_1 V_m}{kT}} - e^{-\frac{\epsilon_1 V_M}{kT}} \right].$$

. . . (8)

Therefore

$$\gamma = \frac{\epsilon_1 R_1}{kT} \cdot \frac{V_M - V_m}{e^{-\frac{\epsilon_1 V_m}{kT}} - e^{-\frac{\epsilon_1 V_M}{kT}}} = \frac{\epsilon_1 R_1}{kT} \cdot W, \quad \dots \dots (9)$$

where

$$W = \frac{V_M - V_m}{e^{-\frac{\epsilon_1 V_m}{kT}} - e^{-\frac{\epsilon_1 V_M}{kT}}}. \quad \dots \dots \dots (10)$$

Substitution of (5) in (1) gives

$$\frac{d^2V}{dx^2} = 4\pi \left(\frac{K}{\rho_1} - \rho_1 \right), \quad . \quad . \quad . \quad (11)$$

and on eliminating ρ_1 by means of (7), we get

$$\frac{1}{4\pi} \frac{d^2V}{dx^2} = \frac{K}{\gamma} e^{\frac{\epsilon_1 V}{kT}} - \gamma e^{-\frac{\epsilon_1 V}{kT}}, \quad . \quad . \quad . \quad (12)$$

the first integral of which is readily obtained as

$$\frac{\gamma \epsilon_1}{8\pi K kT} \left(\frac{dV}{dx} \right)^2 = e^{\frac{\epsilon_1 V}{kT}} + \frac{\gamma^2}{K} e^{-\frac{\epsilon_1 V}{kT}} - C_1, \quad . \quad (13)$$

where C_1 is an integration constant. If the cathode surface, at which V is taken as zero, freely emits electrons, it is necessary, for a steady saturation current of electrons, that $\frac{dV}{dx} = 0$ at that surface, in a manner exactly similar to the way in which the thermionic current from a hot cathode is controlled. Thus V and $\frac{dV}{dx}$ vanish simultaneously; using this fact to evaluate C_1 in (13), we get

$$C_1 = 1 + \frac{\gamma^2}{K}. \quad . \quad . \quad . \quad (14)$$

In a low voltage arc a hot cathode is present and no difficulty is encountered. In an ordinary discharge a surface at which $\frac{dV}{dx}$ vanishes must be taken as the place from which V is measured. The complete solution of (13), after inserting the value of C_1 as given by (14), is

$$\sqrt{\frac{8\pi K kT}{\gamma \epsilon_1}} (x + C_2) = \int \frac{dV}{\sqrt{e^{\frac{\epsilon_1 V}{kT}} + \frac{\gamma^2}{K} e^{-\frac{\epsilon_1 V}{kT}} - \left(1 + \frac{\gamma^2}{K}\right)}}, \quad . \quad . \quad . \quad (15)$$

where C_2 is an integration constant.

If

$$y = e^{\frac{\epsilon_1 V}{kT}} \quad \text{and} \quad H = \frac{\gamma^2}{K},$$

the integral becomes

$$\frac{kT}{\epsilon_1} \int \frac{dy}{\sqrt{y(y+1)(y+H)}},$$

which is a simple elliptic integral expressible in the Jacobian form

$$\frac{2kT}{\epsilon_1} \operatorname{sn}^{-1} \left(\sqrt{\frac{y}{y+H}}, \sqrt{1-H} \right) \quad \text{when } H < 1,$$

$$\text{or } \frac{2kT}{\epsilon_1 \sqrt{H}} \operatorname{sn}^{-1} \left(\sqrt{\frac{y}{y+1}}, \sqrt{\frac{H-1}{H}} \right) \quad \text{when } H > 1.$$

In the two cases respectively, expressing y as a function of x and replacing y by $e^{\frac{\epsilon_1 V}{kT}}$,

$$\left. \begin{aligned} e^{\frac{\epsilon_1 V}{kT}} &= H \operatorname{sc}^2 \left[\sqrt{\frac{2\pi K \epsilon_1}{\gamma kT}} (x + C_2), \sqrt{1-H} \right], \\ e^{\frac{\epsilon_1 V}{kT}} &= \operatorname{sc}^2 \left[\sqrt{\frac{2\pi K \epsilon_1 H}{\gamma kT}} (x + C_2), \sqrt{\frac{H-1}{H}} \right], \end{aligned} \right\} \quad (16)$$

where sc is the usual notation for $\frac{\operatorname{sn}}{\operatorname{cn}}$. If $V=0$ when $x=0$, then the corresponding values of C_2 are given by the multiple valued functions

$$\left. \begin{aligned} C_2 &= \sqrt{\frac{\gamma kT}{2\pi K \epsilon_1}} \operatorname{sc}^{-1} \left(\frac{1}{\sqrt{H}}, \sqrt{1-H} \right), \\ C_2 &= \sqrt{\frac{\gamma kT}{2\pi K \epsilon_1 H}} \operatorname{sc}^{-1} \left(1, \sqrt{\frac{H-1}{H}} \right), \end{aligned} \right\} \quad (17)$$

It is evident that the proper value of C_2 cannot be purely real for, if it were, the potential would become infinite periodically at the zeros of $\operatorname{sn} x$ and $\operatorname{cn} x$; (16) shows that unless $H=1$, the potential will be a periodic function of the distance with a real finite period depending upon quantities determining the physical state of the discharge. If the potential is periodic, evidently its derivatives are periodic with the same period. Therefore, the density of positive ions and the places where there occurs a preponderance of recombination of ions will be periodically distributed, thus giving a quantitative explanation of the very regularly striated positive columns and low voltage arcs commonly observed in electrical discharges. As the real period of $\operatorname{sc}(x, r)$ is $4\operatorname{sn}^{-1}(1, r)$, the

distance P between the striations follows from (16), after putting $H = \frac{\gamma^2}{K}$, in the form

$$\left. \begin{aligned} P &= \sqrt{\frac{8k}{\pi\epsilon_1}} \cdot \sqrt{\frac{T\gamma}{K}} \cdot \text{sn}^{-1} \left(1, \sqrt{1 - \frac{\gamma^2}{K}} \right), \\ P &= \sqrt{\frac{8k}{\pi\epsilon_1}} \cdot \sqrt{\frac{T}{\gamma}} \cdot \text{sn}^{-1} \left(1, \sqrt{1 - \frac{K}{\gamma^2}} \right). \end{aligned} \right\} \quad (18)$$

These formulæ are exact. They can be simplified by certain approximations. By taking $V_m = 0$ and noting that V_M is, in most applications, of the order of 10^{-2} , it is seen from (9) that γ is nearly equal to $\frac{\epsilon_1 R_1 V_M}{kT}$, and taking $\epsilon_1 = \epsilon_2 = \epsilon$ (the elementary charge), which is usually the case, (18) becomes

$$\left. \begin{aligned} P &= \frac{1}{\epsilon} \cdot \sqrt{\frac{8}{\pi}} \cdot \sqrt{R_1 V_M} \cdot \sqrt{\frac{d}{q}} \cdot \text{sn}^{-1} \left(1, \sqrt{1 - \frac{\alpha}{q} \left(\frac{R_1 V_M}{kT} \right)^2} \right), \\ P &= \frac{k}{\epsilon} \cdot \sqrt{\frac{8}{\pi}} \cdot \frac{T}{\sqrt{R_2 V_M}} \cdot \text{sn}^{-1} \left(1, \sqrt{1 - \frac{q}{\alpha} \left(\frac{kT}{R_1 V_M} \right)^2} \right). \end{aligned} \right\} \quad (19)$$

If S_2 is the density of negative electricity at the point where ρ_1 takes its average value R_1 , then

$$\frac{q}{\alpha} = \frac{R_1 S_2}{\epsilon^2}; \quad \dots \dots \dots (20)$$

and if ρ_1 and ρ_2 take their average values near the same point, then

$$\frac{q}{\alpha} = \frac{R_1 R_2}{\epsilon^2}, \quad \dots \dots \dots (21)$$

where R_2 is the average density of negative charge. Putting (20) in (19) gives

$$\left. \begin{aligned} P &= \sqrt{\frac{8}{\pi}} \cdot \sqrt{\frac{V_M}{S_2}} \cdot \text{sn}^{-1} \left(1, \sqrt{1 - \frac{R_1}{S_2} \left(\frac{\epsilon V_M}{kT} \right)^2} \right), \\ P &= \sqrt{\frac{8}{\pi}} \cdot \frac{k}{\epsilon} \cdot \frac{T}{\sqrt{R_1 V_M}} \cdot \text{sn}^{-1} \left(1, \sqrt{1 - \frac{S_2}{R_1} \left(\frac{kT}{\epsilon V_M} \right)^2} \right). \end{aligned} \right\} \quad (22)$$

As $\left(\frac{kT}{\epsilon V_M} \right)^2$ is usually of the order 10^{-4} , it is seen that the type of striation given by the second of the formulæ of

(22) is the one of practical importance. Fixing attention on this formula, as $\frac{S_2}{R_1} \left(\frac{kT}{\epsilon V_M} \right)^2$ will usually be small (unless there is an extremely large electron density compared with the density of positive ions), then the modulus

$$\sqrt{1 - \frac{S_2}{R_1} \left(\frac{kT}{\epsilon V_M} \right)^2}$$

is almost equal to unity, thus making the complete integral large. Since, when r is near unity, $\text{sn}^{-1}(1, r)$ is approximately * equal to $\log \frac{4}{\sqrt{1-r^2}}$, the formula for P becomes

$$P = \sqrt{\frac{8}{\pi}} \cdot \frac{k}{\epsilon} \cdot \frac{T}{\sqrt{R_1 V_M}} \cdot \log \left(\frac{4\epsilon V_M}{kT} \sqrt{\frac{R_1}{S_2}} \right), \quad (23)$$

or inserting some numerical values

$$P = 2.58 \times 10^{-7} \cdot \frac{T}{\sqrt{R_1 V_M}} \cdot \log \left(\frac{1.4 \times 10^7 V_M}{T} \cdot \sqrt{\frac{R_1}{S_2}} \right). \quad (24)$$

This formula shows that the distance between the striations should increase almost linearly with the absolute temperature and vary almost inversely as the square root of the partial pressure of the positive ions. If the latter is proportional to the total gas pressure, then P will vary inversely as the square root of the pressure. This variation † is actually frequently observed. The variation with the temperature could be easily tested experimentally. Equation (24) is consistent with Goldstein's law ‡. It is well known that striations are affected near the glass walls of a discharge-tube. This theory would indicate that, besides a temperature effect, if the glass had a catalytic effect on the rate of recombination of the ions, then α would be increased near the walls. As reference to the second formula of (19) will show, an increase in α tends to make the modulus of the complete elliptic integral become nearer to unity, thereby increasing P . This will obviously tend to make the striations concave towards the anode. This is exactly what is observed. In the same way, if a foreign gas either increases the rate of recombination or decreases the rate of formation or both, the distance between

* See Cayley's 'Elliptic Functions,' p. 47 (1896) for an elementary demonstration.

† *E. g.* Willows, Proc. Camb. Phil. Soc. p. 302 (1900).

‡ See J. J. Thomson's 'Conduction of Electricity Through Gases,' p. 465.

the striations will be greater in presence of the impurity. If the impurity has an ionization potential differing markedly from the gas giving the striations the effect can become very important.

The period is independent of the current density as such, but can easily be affected by it by the change caused in q and T . If the temperature is kept constant an increase in q in (19) will tend to decrease the period. This evidently explains the effect of the striations frequently becoming closer together in parts of a discharge tube that are narrower than the rest of the tube. The effect of an increase in the rate of ionization, causing the striations to move closer together, indicates a method of experimentally studying the absorption of ionizing radiation in ionized gas.

If the positive ions move appreciably under the electric field, the general theory becomes extremely complicated. But, if the positive ion current does not vary much with the distance, it is possibly permissible to apply the above theory in a moving coordinate system moving with the positive ions. The qualitative result would presumably be moving striations having the velocity of the positive ions, but many complicating factors would come into play.

LXXXV. *Sound Changes analysed by Records.*—II. *Voice and Violin.* By H. M. BROWNING, *M Sc., Ph.D.**

[Plate XVI.]

IN the first paper †, records of sound changes on the cornet and trumpet were considered with special reference to shakes, turns, and iterated notes. In the present paper, some records of changing notes on the violin and by the human voice are shown, together with records of tuning-forks and motions of the diaphragm as obtained by tapping.

The apparatus shows well the change of type of vibration when the pitch of a note is altered; also when one note follows another quickly enough, the period during which the change is taking place is of considerable duration and in all cases is clearly visible. The transition is found to be a slur in all the sung passages, and a jump when one note on a violin is followed by another. This is of interest, as in

* Communicated by the Author.

† "Sound Changes analysed by Records," *Phil. Mag.* vol. l. Nov. 1925.

several cases the sung notes were supposed to be separated by a jump.

The present work has been most useful in emphasizing two things which are necessary in order to obtain good quantitative results of the sounds emitted by the violin. The first is to do away with the human element, and this can be done by mechanical bowing and fingering. The second is to obtain a more sensitive diaphragm, which, although selective, will be sensitive to all the harmonics of a certain fundamental tone, and which will be capable of alteration by change of tension to whatever note is required. In a later research it is proposed to use the apparatus as mentioned above to compare the motions of the string with the sound waves produced in the air by the whole violin.

Theory.—A violin is a much more complicated instrument than a cornet or a trumpet. The latter is essentially an air resonator, whereas the former can be analysed into solid and fluid vibrators, which may act both as forcers and responders.

The strings, when plucked, vibrate with frequencies which are commensurate, and the motion can be represented by the Fourier Series:—

$$f(x) = y = \sum_0^{\infty} a_n \sin \frac{n\pi x}{l} \cos \frac{n\pi x}{l} \sin pt, \quad . \quad . \quad (1)$$

where the value of a_n can be obtained from a knowledge of $f(x)$ for a particular instant of time.

The belly of the violin is asymmetrical, therefore the equation of motion for its free vibration must be of the type

$$\ddot{y} + 2k\dot{y} + p^2y + by^2 = 0. \quad . \quad . \quad . \quad (2)$$

The solution of this is a harmonic series the frequency of the fundamental differing from $\frac{p}{2\pi}$ by an amount depending upon b and k .

The bridge may be considered as part of the belly, the motion being conveyed by it from the string to the whole resonance chamber. The air inside is still another vibrating system, but it has such a large damping factor that it will follow the vibration of the wood almost as soon as the sound begins.

The equations of motion of vibrations produced at the

bridge when the string vibrates may be written as follows :—

$$\left. \begin{aligned} &\frac{d^2 y_1}{dt^2} + 2k \frac{dy_1}{dt} + p^2 y_1 = f_1 \sin(nt + \phi_1) \\ & \\ &\frac{d^2 y_m}{dt^2} + 2k \frac{dy_m}{dt} + (mp + h_m)^2 y_m = f_m \sin(mnt + \phi_m) \\ &. \end{aligned} \right\} \quad (3)$$

This is true for small vibrations, and near the bridge of a violin they certainly are small. Each of these equations will have solutions involving two terms, one, a vibration of frequency equal to that of the forcer, and the other of frequency due to the free vibrations. The latter, being damped, will only be present during the formation of the sound. Thus the motion of the belly and also the air will quickly settle down to a series of commensurate partials of the same frequency as those emitted by the string. However, the amplitudes of these partials will not bear the same relation to one another as those of the string, but will be greater or less as the free period of the belly is near or far away from that of the particular partial.

The motion of the air will be recorded by the diaphragm, but, since the motion of the diaphragm is due to resonance, during the establishment of the vibration the free periods of motion will be present as well as the vibrations forced on it from the air. Because of this the change from one note to another may appear longer than it actually is, as the free vibrations of the diaphragm will persist after the free vibration of the air has died out.

The human voice presents a case similar to that of a trumpet, the larynx in the former having the same function as the lips in the latter. The mouth and nasal resonators act as the tube of the trumpet, and the tongue, palate, etc. form the required space for resonance to different notes.

The tuning-forks were made to vibrate with as large a displacement as possible, thus, because of this and also because of their asymmetry and that of the diaphragm, in many cases the octave and higher harmonics appear.

Experimental Arrangement and Results.—The same experimental arrangement was used as in the cases of the trumpet and the cornet*, but a liliput arc was substituted for the

* "Sound Changes analysed by Records," *Phil. Mag.* vol. 1. Nov. 1925.

pointolite ; thus a more intense beam of light was obtained. The motion of the drum carrying the photographic film was found to have a nearly constant velocity, so that distances measured along the films may be taken as proportional to the time for that portion to pass the slit.

Records were obtained on different days, by tapping the film with a lead shot, and it was found that the fundamental frequency altered with atmospheric conditions. Figs. 1 and 2 (Pl. XVI.) show this. Figs. 3 and 4 are caused by banging the table and by clapping the hands. Fig. 4 shows clearly that a violent motion of the air near the diaphragm does not affect it more than a gentle tap with a lead shot. Thus it may be concluded that the free vibrations of the diaphragm which occur at the start of a note are of comparatively short duration.

If figs. 5 and 2 are compared, it will be noticed that the vibration in 2 is damped out in about five centimetres, whereas in 5, which is the record of a plucked violin string of frequency 192 per sec., the free vibrations have not entirely disappeared until 20 cm. are passed. Thus it may be concluded that at least three quarters of the damping effect is due to the violin, and not to the diaphragm. In cases where the initial amplitude is small, the damping due to the diaphragm will be still less marked.

Several records of the vibration of tuning-forks were taken to try to obtain some information as to the motion of the diaphragm. These records were analysed by Mader's Harmonic Analyser to find what overtones were present. Further, certain plucked and bowed notes on the violin were also analysed. A table below shows the ratio of the harmonics to the fundamental in various cases. Figs. 6 and 7 are records of a tuning-fork of frequency 128 per sec., with and without resonance box. Fig. 8 shows the vibration of 256 fork when far from the diaphragm and then brought near to it; the record clearly indicates the overtones produced in the diaphragm by large vibrations. Fig 9 is a record of the vibration of 512 fork, and the motion appears simple harmonic. The lower trace in fig. 10 and fig. 11 show records of a violin string tuned to C' 512 vibrations per sec., in the first case plucked and in the second bowed. The type of vibration alters from one record to the other. The plucked note shows decided harmonics, whereas the bowed note appears to contain only simple harmonic vibrations.

Figs. 12 and 13 are records of the bowing and plucking of the G string (192 per sec.). In all of these overtones are

present, but the amplitude varies in the different cases. The note G appears in later records of bowing, and again the type of vibration is very much like that of fig. 12. The vibration obtained by plucking the string seems to settle down to a smoother type as shown by fig. 12. Fig. 13 is interesting, as it shows a very pronounced second overtone; this must be due to the pressure applied in bowing the string, and forms a strong advocate for mechanical bowing.

TABLE.

Instrument.	Freq. of Note.	Ratio	1st Overtone. Fundamental.	2nd Ov. Fund.	Remarks.
Fork with box.....	128		·057	nil.	
Fork without box ...	128		·1014	·009	
Small Fork	256		·151	·0158	Far from diaphragm.
" "	"		·323	·093	Near diaphragm.
" "	512		·053	nil.	
Violin String (<i>p</i>)* ...	512		·22	·12	
" " (<i>b</i>) ...	512		·19	·05	
" " (<i>p</i>) ...	192		3·8	2·3	
" " (<i>b</i>) ...	192		5·5	5·2	
" " (<i>p</i>) ...	384	{	1·05	·31	At beginning.
" " (<i>b</i>) ...	384		·54	·07	Later.
" " (<i>b</i>) ...	384		·8	0	

* *p* means plucked, *b* means bowed.

The table seems to show that the fundamental of the lowest note on the violin is weak compared with its first and second overtones, and for some of the other notes the overtones are as powerful as the fundamental. Records of tuning-forks vibrating 320 and 384 per second show very little trace of overtones, so it is to be concluded that they are not produced in the diaphragm because of its asymmetry.

Fig. 14 shows A string (427 per sec.) and G string (192 per sec.) plucked successively. The vibration of the upper string had not quite died out when the lower one was started, and it may be this that gives the effect of a wandering overtone (*i. e.* one not quite in tune with the octave of the fundamental) to the vibration of the plucked G string. Fig. 15 shows A (213 per sec.) and G (192 per sec.) bowed successively on the same string, and fig. 16 shows D (288 per sec.) and G (192 per sec.) bowed successively on different strings. The two final notes give traces of approximately the same

form, and the fundamental is again seen to be small compared with the overtones. The first notes, D and A, are very different in type, the upper one showing one overtone and the lower one showing many, with the fundamental obscure. On the same string the change from one note to the other was accomplished in $\frac{1}{9}$ sec., *i.e.* twenty-one vibrations of frequency 192 per second. On different strings the complete change took three times as long. This is due to the vibration of the first string continuing after the bow has left it, so, when the second note begins, which is not for some time after the bow has left the first string, the first note is still sounding, and so distorts the wave due to the second note. Moreover, free vibrations of the string, belly, and diaphragm have to be damped out before the pure forced vibrations of the second string are established. In the first case all these factors are not present, one string giving both notes, there can be no distortion due to the first note persisting after the second is established.

Figs. 17 and 18 show note-changes made by singing. In the first case the change is from a lower note B (480 per sec.) to a higher one D \sharp (600 per sec.). In the second case the change is downward from C (512 per sec.) to G (384 per sec.). In both cases the amplitude is seen to fluctuate during the change. The voice moves by small steps from one note to the other, the time taken to establish the second note being in each case about one-fifth of a second. In the case of the violin changing from one note to another there is no sign of slurring between the notes.

Figs. 19 and 20 are traces of portamento from G (768 per sec.) to C (512 per sec.); the first was obtained on the E string of a violin tuned to C, and the second by the human voice. It was thought that the amplitude of the vibration might be a function of the frequency, but response curves plotted between frequencies and amplitudes in the two cases gave entirely different results. In all probability the change of amplitude is partly due to change of intensity in producing the note.

Figs. 21, 22, and 23 are attempted shakes. The first was obtained by the human voice on B (480 per sec.) and C (512 per sec.). Measuring up the curve it was found that ten notes per second were produced, but there was no definition between the successive notes, a slurring from one to the other being noticed as in the cases of jumping from one note to another. Further, the correct frequency of the higher note was not attained every time, being in most cases slightly sharp.

The second and third are bowed notes on the violin, the

second being on A (213 per sec.) and B (240 per sec.) on the G string, and the third being on B (480 per sec.) and C (512 per sec.) on the A string. The records show in the case of the lower notes a change from A to B after one-fifth of a second, and a change back to A after one-tenth of a second—but not a quick continuous shake. The higher notes do not give a true shake either, the change in the shape of the curve showing where one note passes to another.

Fig. 24 is a record of a turn sung on C; the notes were intended to be C (512), D (576), C (512), B (480), and C (512 per sec.). According to measurement, there is a longer pause on the lowest note than on the other notes, and the turn is wider than it should be, B \flat being reached.

Fig. 25 is the record of a tremolo sung on \overline{EE} on C (512) the fluctuation of amplitude being well marked but irregular. The average number of changes of amplitude are about ten per second.

Conclusion.—With the apparatus as at present used, one person must produce the sounds while another exposes a film at the required time. I wish to thank Mr. T. R. Allitt for help in playing the violin and developing the films, and Mr. H. E. Beckett for his help with records of voice and tuning-forks. The author sang all the vocal passages produced in the paper.

Nottingham,
July 15th, 1926.

LXXXVI. *The Joule-Thomson Effect for Air.* By N. EUMORFOPOULOS. *Fellow of University College, London, and J. RAI, Lieutenant in the Imperial Japanese Navy* *.

THE experiments of which a description is given below were undertaken with the object of determining the thermodynamic correction to the gas thermometer. They were begun in 1910, but it was not until the early part of 1914 that the most suitable material (alundum) was decided on. Owing to the Great War and other circumstances the experiments were suspended for some years, but taken up again about two years ago. It has been thought preferable to publish them at the present stage, as one of us (J. R.) has been obliged to leave England, although experiments have so

* Communicated by Prof. A. W. Porter, D.Sc., F.R.S.

far been carried out only at two temperatures, viz., at 20°C . and at 100°C .

The Porous Plug Experiment, as it has been called, consists in forcing gas through a porous plug and measuring the difference of temperature of the gas on the two sides of the plug. In the case of air there is a cooling effect at ordinary temperatures and pressures. Owing to the narrowness of the channels in the plug the increase of the kinetic energy of the gas while passing through them may cause the temperature there to be considerably below that of the gas on either side of the plug. There will thus be a conduction of heat parallel to the direction of flow. This, however, will not alter the temperature of the gas, once the steady state is set up. It is far otherwise with the heat conducted *across* the direction of flow. This quantity must either be allowed for or made negligibly small. Joule and Thomson allowed for it by assuming that it was proportional to the difference of temperature between the issuing gas and the bath in which the plug was immersed, and inversely proportional to the mass of gas flowing in the unit of time. The published statements do not, however, furnish sufficient information as to the exact way in which these subsidiary experiments were carried out. Heating the bath, as Joule and Thomson did, must certainly disturb the distribution of temperature and lead to an erroneous result. To diminish this correction it is necessary to make the plug as thin as possible.

The disturbance caused by the inevitable fluctuations of pressure is, we think, largely diminished by making the thermal capacity of the plug and thermometers as small as possible. For this reason, as well as for others, we have used thermo-electric junctions in preference to platinum thermometers.

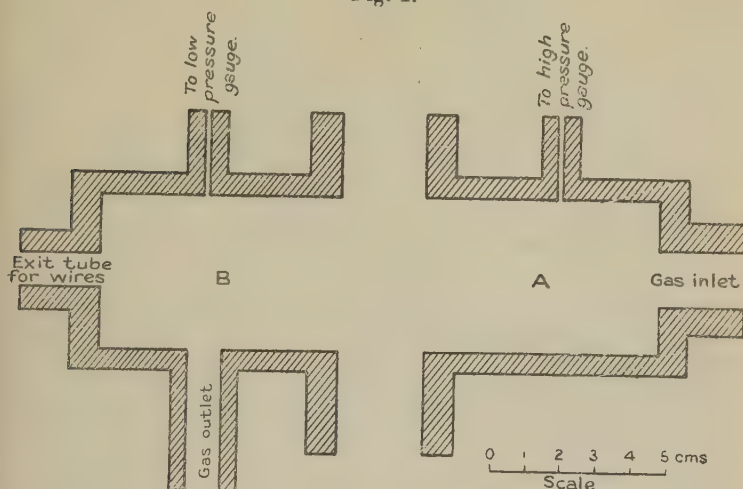
DESCRIPTION OF THE APPARATUS.

The apparatus has been designed to measure the Joule-Thomson Effect at the ordinary temperature and at the temperature of boiling liquids. Atmospheric air is dried by passing through layers of soda-lime and calcium chloride and then passes into an electrically-driven water-cooled pump. A by-pass, controlled by a needle-valve, between the inlet and outlet tubes of the pump enables the latter to be worked at a reasonable speed even at low pressures. From the pump the air passes into a reservoir of 25 litres capacity, through a second drying cylinder, and through a U-tube containing cotton-wool. From this last tube the air passes through two

heating baths, the first one normally contains oil, while the second one is a vapour-bath. Actual experiment has shown that these two baths are amply sufficient for the largest circulation the pump will give. From the second bath the gas passes directly into a third double-jacketed heater containing the plug-box, the double-jacketing being of the same nature as is used in an ordinary hypsometer. From the plug-box the gas passes through a small U-tube containing cotton-wool, through a water-cooled reservoir of 25 litres capacity, and so back to the pump.

To return to the plug-box. Figure 1 gives a diagrammatic representation of the one used.

Fig. 1.



The plug is cemented in the brass holder shown in fig. 2, which is placed between A and B of fig. 1; A, B, and the plug-holder are then screwed together by bolts passing through the flanges of A and B.

The thermo-electric wires are not shown in the figure.

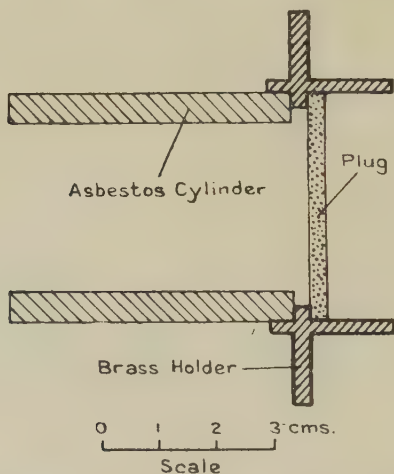
It will be noticed that in the centre of the plug the gas does not come into contact with any metal with the exception of the thermo-electric wires.

The high-pressure gauge (a Dewrance gauge) can be read to the hundredth part of an atmosphere, and was calibrated at the National Physical Laboratory.

It has already been stated that temperatures were measured with thermo-electric junctions. Three copper-constantan junctions (gauges Nos. 40 and 36 resp.) on each side of the

plug are arranged in series, the wires being passed through, and cemented in, the material of the plug itself. The wires project horizontally about 5 cm. into the air space to the right and left of the plug as shown in fig. 2, and are then bent back so as to bring the junctions within a millimetre or

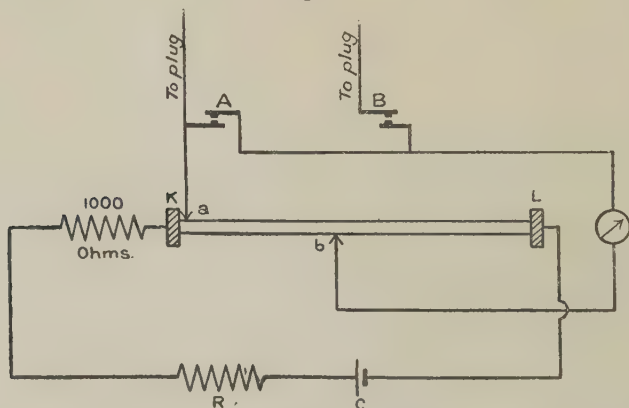
Fig. 2.



two of the surface of the plug. The two copper ends of the junctions pass through a stuffing-box and thence to the potentiometer.

The calibrated potentiometer KL consists of two No. 20 manganin wires connected in parallel. On one of these a

Fig. 3.



permanent junction is made (a in fig. 3), while the slider b is moved on the other until a balance is obtained. The

whole arrangement may thus be represented diagrammatically as follows (the Weston cell circuit is omitted) :—

The resistance R is adjustable, while the Weston cell is balanced on the 1000 ohm coil. The two keys A and B are entirely of copper, and enclosed in two asbestos-lagged boxes. Contact is made by screwing down from the outside a wooden screw bearing on ebonite. These keys have been found thoroughly satisfactory. Great care has been taken in insulating the whole circuit from earth currents.

As the temperature of the air passing through the plug does not remain absolutely constant, the following method of observation has been adopted. The key B is closed (A being open), the slider b having been already adjusted to the approximately correct balancing-point. Galvanometer readings are then taken at regular intervals for some minutes, the pressure being similarly read, and the means taken. Owing to the temperature variation in the room, there will always be some stray e.m.f. in the circuit. To evaluate this, immediately after the above observations have been taken, B is broken, C is disconnected, and then A is made, the slider remaining untouched. The deflexion so obtained is taken as a measure of the stray e.m.f. The potentiometer zero is obtained by moving the slider b to a position opposite a with B open and A closed (C being, of course, connected). The stray e.m.f. is measured in this case also. These four measurements are carried out in each observation. The galvanometer sensitiveness (for the interpretation of the meaning of small deflexions) is taken each day. Two measurements of sensitiveness are required—one for the main experiment, and the other for the stray e.m.f., as the resistance of the circuit in the latter case is smaller. Part of the stray e.m.f. arises in the galvanometer itself, and has been much diminished by careful shielding.

It must not be supposed that the pressure fluctuations cause the galvanometer readings to vary to any very large extent, while observations are being made on the Joule-Thomson effect. When one of the thin plugs referred to below is being used, the largest variation in the readings only amounts to some three millimetres of the galvanometer (say $\cdot 005$ dgr.), even when the pressure difference is small. When a thicker plug is used (Plug No. 3 referred to later), the variations at low pressure differences may be as much as five times the above quantities, but this is a somewhat extreme case.

The thermo-electric e.m.f. of the couple used was determined directly on the potentiometer. The pressure effect on this e.m.f. was tested and found to be negligible for present

purposes. The bridge-readings given later can be converted into degrees by multiplying by $\cdot 02977$ in case of observations at 20° and by $\cdot 02570$ for observations at 100°C .

THE EXPERIMENTS.

As has already been stated the substance ultimately decided on was alundum, which is made in different porosities, the densest being RA 84. Unless otherwise stated, it is to be understood that the plug used was made of this material and was cemented, in the form of a disk, in the holder shown in fig. 2. It had been hoped that, by making the conduction correction very small, it would be sufficiently accurate to apply the Joule-Thomson method of correction. This accounts for the multiplicity of readings at low pressures. It will be seen that our hope has not been fulfilled.

In the following tables, P_2 indicates the pressure in atmospheres on the high-pressure side of the plug, P_1 that on the low-pressure side, v the volume of air passing through the plug in c.c./sec. measured at the ordinary temperature and pressure (a rough measurement), and L the bridge reading in cms.

Plug No. 3.

This plug is 42 mm. in diameter and 6 mm. thick. The outer portion had been glazed, leaving a central porous portion 25 mm. in diameter. Besides the asbestos tube shown in fig. 2 (which is present in all cases), the protection against conduction of heat consisted of a short glass tube (diam. 27 mm.) cemented on to the disk, and a second one (diam. 15 mm.) within this cutting off a guard-ring.

May 15, 16, 19, & 20, 1924. Observations reduced to 20°C .

P_2	P_1	$P_2 - P_1$	L	v
10.93	1.21	9.72	77.31	1470
9.87	1.16	8.71	69.24	1275
8.91	1.15	7.76	62.21	1100
8.06	1.11	6.95	56.18	957
6.89	1.08	5.81	47.21	756
5.98	1.06	4.92	39.95	600
5.03	1.04	3.99	31.63	447
4.05	1.02	3.03	23.10	301
3.00	1.01	1.99	12.24	169
2.94	1.00	1.04	4.21	74
1.70	1.00	0.70	1.98	45
2.98	1.01	1.97	11.88	168
4.72	1.03	3.69	28.59	401
7.08	1.08	6.00	49.25	790
9.20	1.15	8.05	64.96	1153
10.68	1.20	9.48	75.38	1423
7.05	1.08	5.97	48.51	784

These results will be found plotted on diagram 3.

Within the limit of our pressure range the Joule-Thomson effect can be represented by a formula of two terms :

$$a(P_2 - P_1) + b(P_2^2 - P_1^2).$$

If we could also assume, with Joule and Thomson, that the conduction effect is proportional to the temperature difference and inversely proportional to the quantity of gas flowing in a given time through the plug, then

$$a(P_2 - P_1) + b(P_2^2 - P_1^2) = L + c \frac{L}{v},$$

where c is some constant. When the formula is applied to the experimental results as is done below, it is found that the value of c is not constant.

It is obvious that, given enough experimental points, a , b , and c can all be determined, and such calculations have been carried out by the method of least squares with all the results communicated in this paper.

With this plug the conduction is somewhat serious. Taking the points up to a pressure difference of 4 atmospheres, the value of c is found to be 115 c.c. If, however, the other ten observations of the above table are used, the value of c is only 49 c.c. This diminution in the value of c as the pressure difference is increased is repeated with all the plugs used, without exception.

February 11 & 12, 1926. Observations reduced to 100° C.

P_2 .	P_1 .	$P_2 - P_1$.	L .
10.87	1.13	9.74	52.14
10.00	1.11	8.89	47.91
8.97	1.09	7.89	42.95
8.02	1.07	6.95	37.97
7.00	1.05	5.95	32.84
6.00	1.03	4.97	26.79
5.00	1.02	3.98	20.32
4.04	1.01	3.03	13.93
3.07	1.01	2.06	7.20
2.50	1.00	1.50	4.18
1.72	1.00	0.72	0.67

These results will be found plotted on diagram 4.

Plug No. 2.

Disk identical in construction with No. 3, but only 3 mm. thick. Two concentric asbestos-paper tubes, about a cm. in length, were arranged on the low-pressure side, thus cutting off guard-rings.

June 4, 5, & 6, 1924. Observations reduced to 20° C.

P_2	P_1	$P_2 - P_1$	L	v
10.05	1.23	8.82	70.11	1555
8.86	1.16	7.70	61.18	1317
8.11	1.15	6.96	56.09	1161
7.09	1.12	5.97	47.83	959
5.82	1.08	4.74	37.76	710
4.99	1.06	3.93	31.34	554
3.93	1.03	2.90	22.51	372
2.95	1.01	1.94	13.77	228
1.99	1.00	0.99	5.34	94
1.72	1.00	0.72	3.87	62
3.22	1.01	2.21	15.99	260
4.09	1.03	3.06	24.16	399

These points are plotted on diagram 3.

Calculation of c from all points above 3 atmospheres pressure difference gives a value of 36 c.c. On examining diagram 3 it will be found that while for the lowest pressure observed the conduction correction for plug No. 3 is about twice that for plug No. 2, the difference has practically disappeared by the time we get to a pressure difference of 5 atmospheres.

As the plugs just described gave, at low pressures, too high a conduction effect, it was decided to try disks with a thickness of 1 to 2 mm. only. These, if 4 cm. in diameter, would not be strong enough to support a pressure of 10 atmospheres, so a thick alundum ring was cemented in the holder (fig. 2). This ring carried the thermo-electric wires, and was glazed or cemented so as to be non-porous. The inside edge of the ring was bevelled so as to hold securely the disk, which was cemented in place. It will be seen shortly that most of these disks were so porous that a correction has to be made for the kinetic energy of the air on the low-pressure side. It is assumed that no part of this energy is converted into heat on moving past the wires. The correction is occasionally large, and is thus open to some uncertainty.

Plug No. 5.

It was decided to try the effect of different methods of heat insulation. A porous disk of 2 cm. diameter and 1 mm. thickness was fixed as just described. On the low-pressure side an asbestos cylinder of the same diameter was cemented to the plug. As only comparative results were aimed at, the kinetic energy correction, although appreciable, has not been applied. Observations were made on May 28 and June 9, 1925. These will be found plotted on diagram 1.

Asbestos wool was now packed between the two asbestos cylinders. With the plug in this condition observations were made on June 11, which will be found plotted on the same diagram. A small, though noticeable, improvement has been produced in bringing the low-pressure values into line with the high-pressure ones.

After this, a cylinder, about 1 cm. in length and the same in diameter, made of asbestos paper, was fixed on the low-pressure side; the air outside this cylinder was thus made to act as a guard-ring. The observations made on June 22 (see diagram) show that a great improvement has been obtained, which is especially noticeable at low pressures.

In all these cases the junctions were, as has already been stated, within a millimetre or two of the plug. They were now moved about 1 cm. away from the plug on the low-pressure side. This would bring them about level with the opening of the asbestos tube added for the observations on June 22. Results were obtained on June 25 with the plug in the altered condition. From the diagram it will be seen that the last change has produced but a small effect. This experiment shows that with the guard-ring the heat insulation is quite satisfactory, once the gas has passed through the plug.

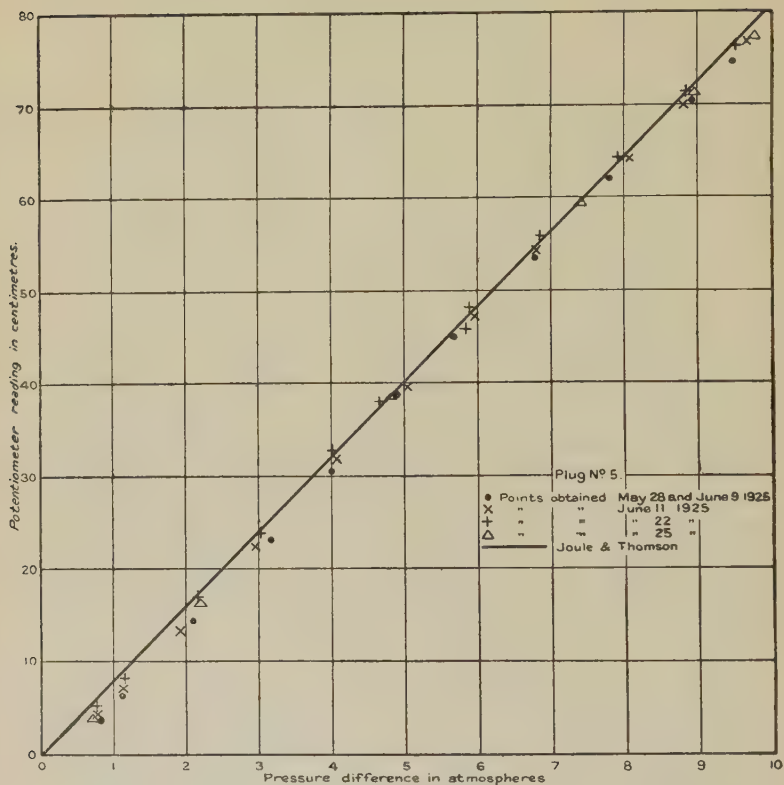
With such a disk the following measurements were taken:—

August 7, 1925. Observations reduced to 20° C.

P_2 .	P_1 .	$P_2 - P_1$.	L .	v .	L corrected.
10.76	1.17	9.59	75.78	1553	74.85
8.61	1.12	7.49	60.07	1169	59.49
6.89	1.08	5.81	47.01	867	46.66
5.42	1.05	4.37	35.24	609	35.06
3.98	1.03	2.95	23.71	374	23.64
3.20	1.02	2.18	17.07	261	17.03
2.17	1.01	1.16	8.34	122	8.33
1.82	1.00	0.82	5.43	82	5.43
10.68	1.17	9.51	75.74	1540	74.82
9.05	1.13	7.92	63.42	1248	62.77

The last column is the fourth column corrected for kinetic energy as already explained. The above points are indicated on diagram 3. The method of least squares applied to the five lowest points gives for c a value of 19 c.c., while the seven highest give 13.5.

DIAGRAM 1.



August 10 & 11, 1925. Observations reduced to 100°C .

P_2	P_1	$P_2 - P_1$	L.	v .	L corrected.
10.76	1.17	9.59	50.62	1453	49.05
8.59	1.11	7.48	40.00	1085	39.03
7.08	1.08	6.00	32.81	825	32.21
5.73	1.05	4.68	25.28	602	24.95
4.07	1.02	3.05	16.23	355	16.11
3.01	1.01	2.00	10.23	213	10.19
2.24	1.01	1.23	5.82	119	5.81
1.84	1.00	0.84	3.55	76	3.54
10.77	1.17	9.60	50.94	1455	49.37
9.67	1.14	8.53	45.60	1267	44.35
8.30	1.10	7.20	38.14	1035	37.24
6.34	1.05	5.29	28.97	704	28.51
5.09	1.04	4.05	21.62	498	21.39
3.48	1.02	2.46	12.91	272	12.84
2.29	1.01	1.28	6.33	125	6.31
1.85	1.00	0.85	3.58	78	3.57
7.77	1.09	6.68	35.90	945	35.14

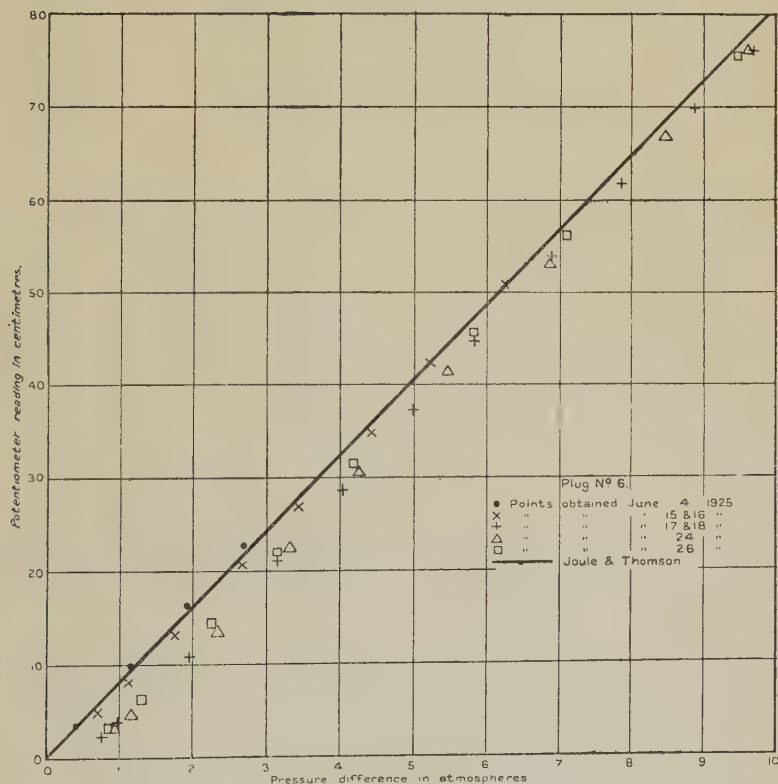
For curve see diagram 4.

The method of least squares applied to the seven lowest points gives for c a value of 25 c.c., while the eleven highest give 11.5.

Plug No. 4.

An attempt was made to diminish the conduction effect by supporting the disks on uralite rings cemented to the thick

DIAGRAM 2.



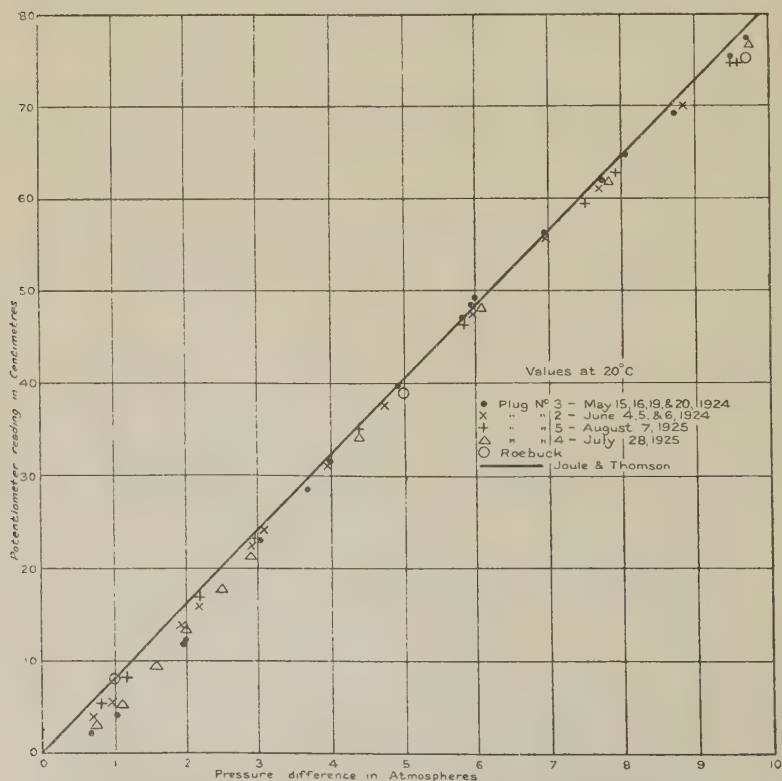
alundum ring. The result is not altogether successful—the favourable effect of the uralite is no doubt neutralized by the additional cement that had to be employed. A somewhat different way of mounting on the uralite might be more successful.

July 28, 1925. Observations reduced to 20° C.

P_2	P_1	$P_2 - P_1$	L	v	L corrected.
1.78	1.00	0.78	3.23	55	3.23
2.09	1.01	1.08	5.82	82	5.81
3.00	1.01	1.99	13.55	167	13.52
3.90	1.02	2.88	21.48	262	21.42
5.41	1.03	4.38	34.60	445	34.43
7.09	1.05	6.04	48.52	662	48.15
8.88	1.08	7.80	62.52	899	61.85
10.82	1.11	9.71	77.75	1194	76.65
3.48	1.01	2.47	17.90	217	17.86
2.58	1.01	1.57	9.75	126	9.73

These points will be found plotted on diagram 3.

DIAGRAM 3.



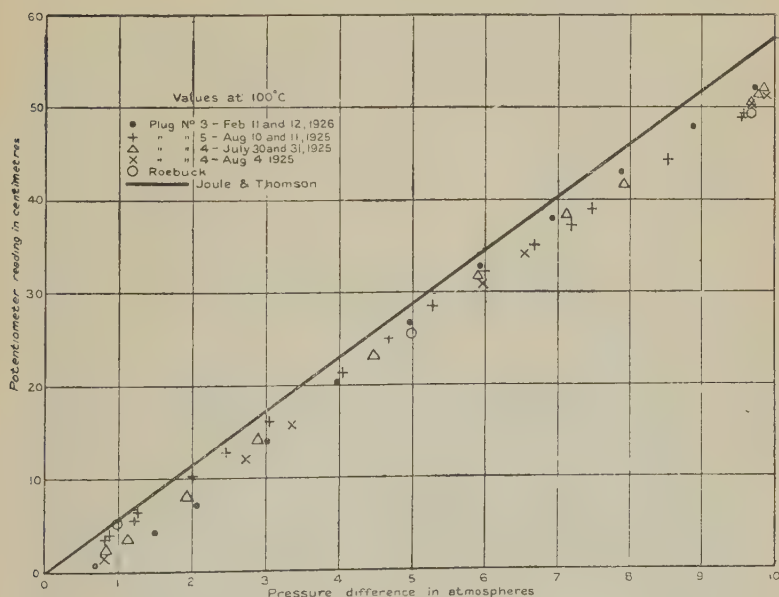
The method of least squares applied to all the points gives for c a value of 61 c.c., while, if applied to the six highest points only, we get a value of 48.

July 30 & 31, 1925. Observations reduced to 100° C.

P_2	P_1	$P_2 - P_1$	L	v	L corrected.
10.78	1.09	9.69	52.11	966	50.71
8.97	1.06	7.91	42.61	753	41.70
6.97	1.04	5.93	32.22	529	31.76
5.50	1.03	4.47	23.50	371	23.27
3.90	1.01	2.89	14.20	216	14.12
2.94	1.01	1.93	8.04	133	8.01
2.14	1.01	1.13	3.83	70	3.82
1.84	1.00	0.84	2.27	47	2.27
10.88	1.10	9.78	52.55	975	51.13
8.18	1.05	7.13	38.87	664	38.16
10.95	1.10	9.85	52.92	984	51.47

These points are plotted on diagram 4. From the eight highest points the value of c is 53 c.c.

DIAGRAM 4.



After the above measurements were taken, a little alundum powder was suspended in water; the larger particles were allowed to settle, and then some of the water was passed through the disk so as to diminish the porosity. Experiments carried out on August 4 will be found plotted on the same diagram.

Plug No. 6.

In this case a very porous plug was experimented on, and its porosity diminished by successive additions of fine alundum cement, as in the last case. A disk of RA 225 was accordingly set up (diameter 2 cm., thickness 1.6 mm.) with an asbestos tube 2 cm. in diameter, but no guard-ring. The results will be found plotted on diagram 2. In the observations on June 4, 1925, the highest pressure the pump would give was 4 atmospheres, the low pressure registering 1.31 atm. No kinetic energy correction has been applied.

After a first treatment with alundum powder observations were made on June 15 and 16. After a further treatment with alundum measurements were made on June 17 and 18. On June 24 further readings were taken, after asbestos wool was packed between the two asbestos tubes, and finally on June 26 a guard-ring was placed in position. These values are shown on diagram 2.

DISCUSSION OF THE RESULTS.

On turning to Joule and Thomson's original experiments to see if the conduction correction is satisfactory, we find eight measurements in the neighbourhood of 7°. On reducing these to the same temperature, but before applying the correction under discussion, we find an extreme variation of 4 per cent. This is *increased* to 6 per cent. after the correction is applied, while the highest numbers are those to which the largest correction has been applied (11 or 12 per cent.). The values round about 92° show the same effect, but the numbers are too variable for much stress to be laid on them.

In view of what we have said about the constant diminution of c with increase of pressure, it becomes a question whether, at the high pressures, there is any appreciable conduction correction to apply. On examining the curves in diagram 3 it will be noticed that, however much they may differ initially, they all seem to coincide from a pressure difference of, say, 5 atmospheres upwards. This is confirmed by the results plotted on diagrams 1 and 2. Taking these, as seems justifiable, to give the true values we get the following expression for the Joule-Thomson effect for air at 20° C. (in degrees centigrade) :

$$\cdot 2492(P_2 - P_1) - \cdot 0012_8(P_2^2 - P_1^2).$$

Similarly the value at 100° is :

$$\cdot 1453(P_2 - P_1) - \cdot 0009_5(P_2^2 - P_1^2).$$

While this paper was being written, a communication by Roebuck has appeared on the Joule-Thomson effect in air (Proc. Amer. Acad. lx. p. 537). This observer has extended his experiments over a wide range (220 atmospheres and 280° C.). The plug is of the "radial flow" type, *i.e.* it consists of a porcelain tube with one end closed; the gas passes from the outside to the inside of the tube, and the temperatures were measured with encased platinum thermometers. On diagrams 3 and 4 three points are plotted from Roebuck's results. It will be seen that his results are slightly lower than ours. It should be added that Roebuck states that his results for low pressures are not as concordant as those obtained for higher pressures.

In conclusion we wish to tender our best thanks to Mr. J. Rose-Innes, who has borne practically the whole expense of the investigation and has otherwise given us much help. We have also to thank Prof. A. W. Porter, F.R.S., for constant advice and assistance. In the first part of the investigation we had the advantage of help from Mr. J. K. Aykroyd, whose engineering knowledge was of great aid in the designing of the apparatus. To him also we wish to express our indebtedness.

LXXXVII. *On Reversal in Vacuum Tube Spectra.*

By T. R. MERTON, F.R.S.*

THE reversal of the spectrum lines of gases which are excited in vacuum tubes has been observed frequently. This effect is to be expected with tubes in which the light from a constricted portion passes through a long region of larger bore and in which in consequence the excitation is less intense. It is also sometimes observed in the conventional type of end-on tube, in which the capillary opens rather abruptly into a wide tube in which the luminosity is in general very small, but in which one may suppose that there are enough excited atoms to exhibit the phenomenon. This effect has been the subject of several investigations on account of its importance in connexion with secondary standards of wave-length. Perard (*C. R.* clxxvi. p. 375, 1923) has found that in certain sources some of the neon lines appear double or even more complex. Buisson and Jausseran (*C. R.* clxxx. p. 505, 1925) state that this is due to

* Communicated by the Author.

reversal, and were unable to observe the effect at right angles to the capillary*. The whole question has recently been discussed by Burns (Journ. Opt. Soc. Amer. xi. No. 4, p. 301, 1925), who concludes that the neon lines are suitable as standards under specified conditions in which the observations are made perpendicular to the capillary. Meissner (*Ann. d. Phys.* lxxvi. p. 124, 1924 ; cf. *Phys. Zeits.* xxvi. p. 687, 1925) has investigated the phenomena of absorption by excited neon, and has found that this is very conspicuous in the case of certain lines which arise from electron transitions terminating in a metastable state. A high resolving power is in general required to observe these reversals directly. I have recently found that this effect can be seen for the D_3 line of helium, not only in long end-on tubes, but also perpendicular to the capillary of a vacuum tube of the conventional pattern if the current density is sufficiently great. The observations were made with an echelon grating having thirty-five plates of glass 15 mm. thick in optical contact, and preliminary analysis was made by means of a constant deviation spectroscope. With an end-on tube about 25 cm. long and of 5 mm. internal bore containing helium at between 5 and 10 mm. pressure the reversal was distinctly seen with quite moderate currents, but it became much more conspicuous when the tube was excited by very heavy currents. The most powerful discharges used were obtained by means of a transformer which raised the voltage of the A.C. supply to 5000 volts, and currents of rather more than 100 milliamperes could be passed through the tube for short periods. With these currents the reversal was very distinct, and appeared to be quite definitely unsymmetrical, the intensity on the more refrangible side of the reversal being somewhat greater. The interpretation of this in so far as the asymmetry is concerned was rendered somewhat uncertain owing to the presence of the fainter component of the D_3 line, since this faint component was not resolved from the next order spectrum of the main line owing to the widths of the lines, the difference in wavelength corresponding to the separation of successive orders being 0.371 \AA , whilst the separation of the components is 0.342 \AA . There was a distinct broadening of the line at high current densities, but the reversal was very narrow. When the tube was excited by a feeble discharge the reversal could not be seen. It is not at once clear why a heavy discharge should be essential to the observation if the reversal

* R. W. Wood (*Phil. Mag.* x. p. 876, 1926) has recently described the phenomena of reversal in long end-on hydrogen tubes.

is due to a less strongly excited layer at the end of the capillary, as it would seem that whatever the current through the tube there must be some region at which the conditions for a reversing layer would obtain. An alternative explanation can perhaps be found in the assumption that the apparent reversal is not due to a reversing *layer* at all. We may perhaps suppose that the final state in the transition which gives rise to the D_3 line possesses some measure of metastability, and that atoms remain in this state until they undergo collisions with other atoms. The faster moving atoms are responsible for the emission or absorption at the outer parts of the line, the width of which is due to the components of the velocities of the atoms in the line of sight, and the greater the velocity of an individual atom the shorter will be its expectation of light in a metastable state. The result of this will be that E/A , the ratio of the emissive to the absorptive power, will be a minimum at the centre of the line, since the absorptive power at a particular wavelength depends on the number of atoms in a metastable state which, in virtue of the component of their velocity in the line of sight can absorb that wave-length. An infinite thickness of the gas would thus show a minimum at the centre of the line, and the observation of this minimum in vacuum-tube spectra will depend on a sufficient thickness of the radiating gas, or alternatively on a high current density. It should therefore be possible to observe the phenomenon perpendicular to the capillary of a vacuum tube with very heavy currents, and the experiment was accordingly tried. The tube contained helium at a few millimetres pressure and the internal bore of the capillary was about 2 millimetres. With moderate currents no effect could be seen, but with very heavy currents the reversal was distinctly visible. It was exceedingly narrow, and was indeed just within the resolving power of the echelon, which was over 500,000 in this part of the spectrum, and could not be seen with a small Lummer Gehrcke plate having a nominal resolving power of 200,000.

The above considerations afford no explanation of the apparent asymmetry, but it is probable that some broadening by the Stark effect is operative at these current densities, and this would cause a widening of the line to the violet, according to the observations of the Stark effect for this line by Takamine and Kokubu (*Mem. Coll. Sci. Kyoto*, iii. p. 9, 1919). It would seem that it may be necessary to specify the internal bore of vacuum tubes and the current density, when they are to be used as sources of lines for standard wave-lengths.

There is doubtless a layer of less strongly excited gas in the neighbourhood of the walls of any vacuum tube; but the fact that the observation of reversal seems to depend on a high current density appears to imply that the existence of this layer is not sufficient to explain the phenomena.

July 31st, 1926.

LXXXVIII. On "Relaxation-Oscillations."

By BALTH. VAN DER POL, Jun., D.Sc.*

1. **T**HE condition of a simple oscillatory system, possessing one degree of freedom and subjected to a dissipative force, may be represented by the well-known linear differential equation

$$\ddot{x} + \alpha \dot{x} + \omega^2 x = 0, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

the solution of which is

$$x = C_1 e^{-\frac{\alpha t}{2}} \sin \left(\sqrt{\omega^2 - \frac{\alpha^2}{4}} t + \phi \right). \quad . \quad . \quad . \quad . \quad (2)$$

If we have also

$$\alpha > 0$$

$$\text{and} \quad \frac{\alpha^2}{4} < \omega^2,$$

the solution (2) represents a damped oscillation with a logarithmic decrement δ given by

$$\frac{\delta}{\pi} = \frac{\alpha}{\omega}.$$

If it happens that the "resistance" in the system is negative, such as may be the case in certain electrical circuits, the sign of α is reversed and (1) becomes

$$\ddot{x} - \alpha \dot{x} + \omega^2 x = 0, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

the solution of which is

$$x = C_1 e^{+\frac{\alpha t}{2}} \sin \left(\sqrt{\omega^2 - \frac{\alpha^2}{4}} t + \phi \right).$$

If, again, we have

$$\alpha > 0$$

$$\text{and} \quad \frac{\alpha^2}{4} < \omega^2,$$

the solution (2 α) represents an oscillation; but in this case the amplitude is gradually increasing instead of decreasing,

* Communicated by the Author.

and the logarithmic decrement of the former case is replaced by a logarithmic increment δ given by

$$\frac{\delta}{\pi} = \frac{\alpha}{\omega}.$$

2. A solution of the form (2a) is, however, physically unrealizable because it indicates an amplitude growing to infinity. Thus for actual physical systems the differential equation (3) will only be valid for values of x up to a certain value. To express the limitation of the amplitude we must assume that the coefficient of the "resistance" term is a function of the amplitude itself, becoming positive at the higher values. Thus we may in (3) replace α by the expression $\alpha - 3\gamma x^2$, where γ is a constant. Hence we obtain instead of (3):

$$\ddot{x} - (\alpha - 3\gamma x^2)\dot{x} + \omega^2 x = 0. \quad (4)$$

This equation has been previously considered* in connexion with the subject of triode oscillations.

Let us now change the units of time and of x and write

$$\text{and } \left. \begin{aligned} \omega t &= t', \\ x &= \sqrt{\frac{\alpha}{3\gamma}} v. \end{aligned} \right\} \quad (4a)$$

Then (4) becomes (after dropping the accents)

$$\frac{d^2 v}{dt^2} - \frac{\alpha}{\omega} (1 - v^2) \frac{dv}{dt} + v = 0. \quad (5)$$

Writing further

$$\frac{\alpha}{\omega} = \epsilon$$

and using fluxional notation we have

$$\ddot{v} - \epsilon(1 - v^2)\dot{v} + v = 0. \quad (6)$$

Now in the usual cases of triode oscillations we know from the experimental data that it takes several periods for the amplitude to build up to the final steady value. Expressed mathematically this means

$$\epsilon \ll 1. \quad (7)$$

* Van der Pol, *Tijdsch. v. h. Ned. Radio Gen.* i. (1920); *Radio Review*, i. p. 701 (1920). Appleton and van der Pol, *Phil. Mag.* xliii. p. 177 (1922). Robb, *Phil. Mag.* xliii. p. 206 (1922).

Recognizing the condition (7) the equation (6) may be solved approximately in the following way :

$$\text{Let} \quad v = a \sin(t + \phi),$$

in which, since the logarithmic increment is small, we may assume a to be a slowly varying function of the time, such that

$$\dot{a} \ll a.$$

On substituting (8) in (6), and omitting small quantities and neglecting higher harmonics, we find that

$$\frac{1}{\epsilon} \frac{da^2}{dt} - a^2 + \frac{1}{4}a^4 = 0,$$

$$\text{or} \quad a^2 = \frac{4}{1 + e^{-\epsilon(t+C)}}.$$

The approximate solution of (6) may therefore be written

$$v = \frac{2 \sin(t + \phi)}{\sqrt{1 + e^{-\epsilon(t+C)}}},$$

which represents an oscillation the amplitude of which at first* increases with time according to the factor $e^{\frac{\epsilon t}{2}}$, but finally approaches the steady value

$$a = 2.$$

Reverting to the original variables of (4) we thus have

$$x = \sqrt{\frac{\alpha}{\frac{3}{4}\gamma}} \cdot \frac{1}{\sqrt{1 + e^{-\alpha(t+C)}}} \cdot \sin(\omega t + \phi). \quad (8)$$

There is, however, a more direct method of finding the steady final amplitude of the oscillations for cases represented by (6). For example, let us assume that a periodic solution of the equation exists. Multiplying (6) throughout by $\int v dt$ and integrating over the (unknown) period we find that

$$\overline{v^2} = \frac{1}{3} \overline{v^4} \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

(the horizontal dashes indicating integration over the period). If now we assume v to be very nearly sinusoidal, *i. e.*

$$v = a \sin t,$$

(9) gives us at once

$$a = 2.$$

* *I. e.*, so long as the amplitude is so small that in (6) the non-linear term ϵv^2 may be neglected in comparison with $-\epsilon \dot{v}$.

To find the time period of the oscillations we multiply (6) by v and again integrate over the (unknown) period. In this case we find that

$$\overline{\dot{v}^2} = \overline{v^2}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

so that, assuming again the solution to be approximately sinusoidal, we find from (10), that the angular frequency is unity.

3. Up to the present we have considered (6) with the supplementary condition

$$\epsilon \ll 1, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

but it is of considerable interest, and also the main object of this paper, to investigate the sequence of events when

$$\epsilon \gg 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7a)$$

It may be noted that even with the new condition (7 a) the equation (6) has a periodic solution, since the relations (9) and (10) are independent of the numerical value of ϵ . Further, on physical grounds, we may expect that there is a periodic solution of (6) when (7 a) holds, as may be seen from the following considerations. For small values of v , (6) may be written approximately as

$$\ddot{v} - \epsilon \dot{v} + v = 0, \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

and this has, when (7 a) holds, an approximate solution

$$v = C_1 e^{\epsilon t} + C_2 e^{\frac{t}{\epsilon}}.$$

The value of v therefore would approach infinity asymptotically so that $v=0$ is not a stable solution. Thus, so long as (11) is valid, we are dealing with the well-known *aperiodic* case, but with negative damping. But when the amplitude increases and $v^2 > 1$, the coefficient of the second term on the left-hand side of (6) becomes positive indicating a positive resistance and therefore a reduction in amplitude with time. Now the limiting values $v = \pm 1$ are not solutions of (6), so that, in general, we may expect the solutions to be periodic, *even when condition (7 a) is fulfilled*. Although for small amplitudes the resistance has such a big negative value that the linear case would be highly aperiodic, the non-linear term in (6), i. e. $v^2 \dot{v}$, makes the solution periodic. We may thus say that we are dealing with a *quasi-aperiodic* solution.

4. It has not been found possible to obtain an approximate analytical solution for (6) with the supplementing

condition (7a), but a graphical solution may easily be found in the following way. If we write

$$\dot{v} = z,$$

(6) may be written

$$\frac{dz}{dv} - \epsilon(1-v^2) + \frac{v}{z} = 0, \quad . \quad . \quad . \quad (12)$$

which is a first order equation of the super-Riccati type. Let us draw in a z, v plane a series of "isoclines," *i. e.* curves connecting all points for which $\frac{dz}{dv}$ is equal to a certain quantity. An example of such isoclines is denoted by

$$\frac{dz}{dv} = C_1$$

where C_1 is a constant so that, combining with (12), we have as expression for an isoclyne:

$$C_1 - \epsilon(1-v^2) + \frac{v}{z} = 0.$$

Several of these isoclines may be drawn in the z, v plane, and we can indicate by means of short lines, as is done in fig. 1, the direction the integral curve must have when it crosses an isoclyne. (For example, this direction for the isoclyne C_1 is given by

$$\frac{dz}{dz} = C_1, \text{ etc.})$$

From a diagram in which the inclinations of the integral curves are marked on the isoclines we may easily draw the integral curves in the z, v plane. This is done in fig. 1 for the value

$$\epsilon = 0.1,$$

and it is seen that the integral curve obtained indicates the track of a point approaching a closed curve after many complete circuits (small increment).

In the same way fig. 2 is drawn for

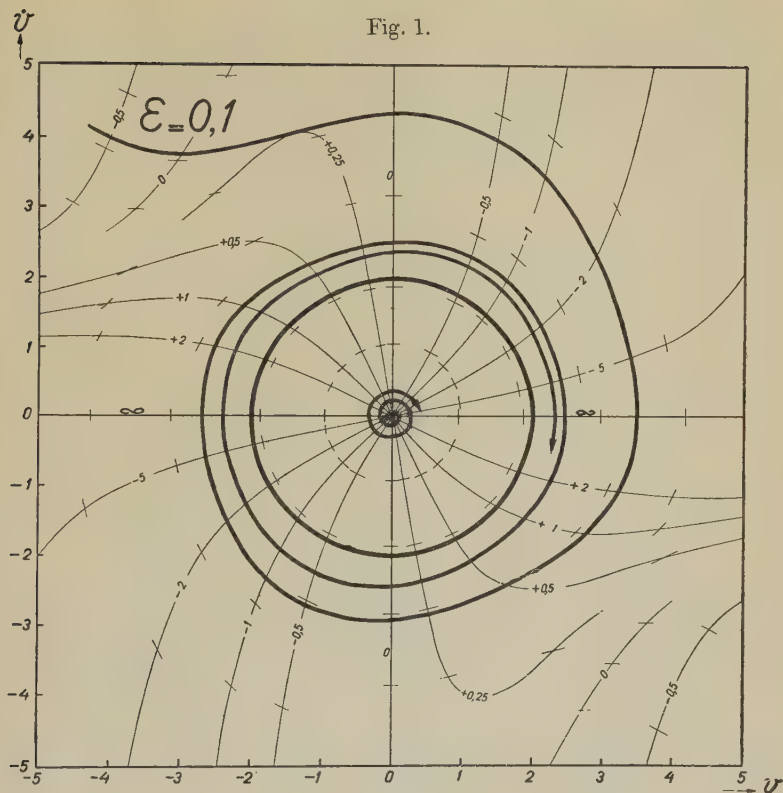
$$\epsilon = 1,$$

and fig. 3 for

$$\epsilon = 10,$$

all three figures showing a closed curve solution. In the

Fig. 1.



case of fig. 3 (quasi-aperiodic case) the final steady closed curve, representing the periodic solution, is practically reached after one revolution only. When the intermediate integral $z=f(v)$ has been obtained in this way it is easy to construct from it in a similar fashion the integral

$$v=\phi(t).$$

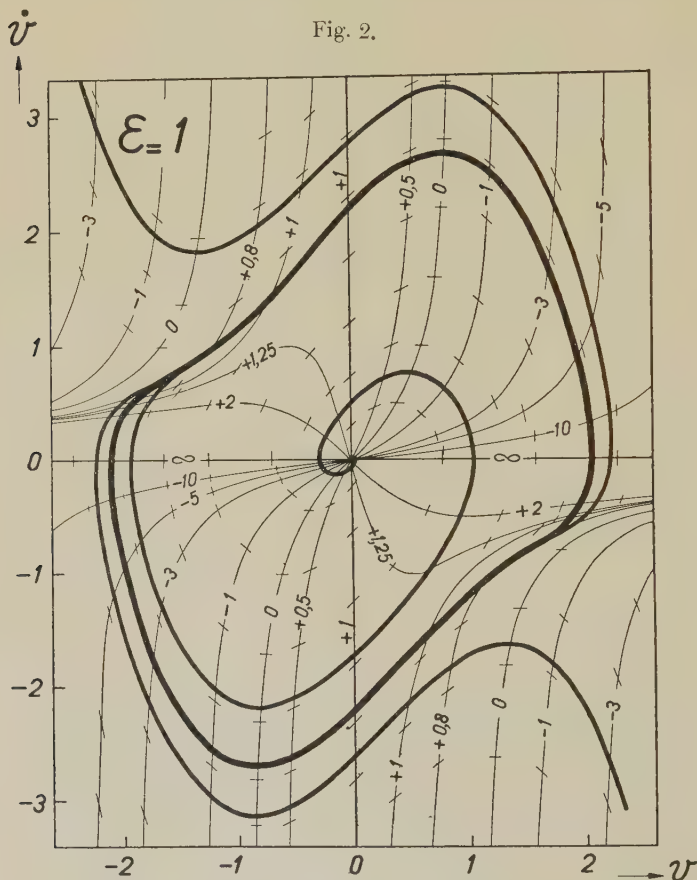
Some examples of such results are exhibited in fig. 4 and represent the solution of (6) for the three cases

$$\epsilon=0.1,$$

$$\epsilon=1,$$

$$\epsilon=10.$$

The first case (small increment) might also have been plotted from the solution (8), and a numerical comparison of the two solutions shows them to be in satisfactory agreement. This case represents a sinusoidal oscillation of gradually increasing amplitude, the value of which is finally



steady and equal to 2. The angular frequency, for the units used, is unity. The second case of fig. 4, (i. e. $\epsilon=1$) indicates a somewhat similar sequence of events, but here the final amplitude is reached in fewer oscillations, while a marked departure from the sinusoidal form is noticed. The third case (i. e. $\epsilon=10$) is particularly interesting. Here it is noticed that the curve first rises asymptotically and after

Fig.3 .

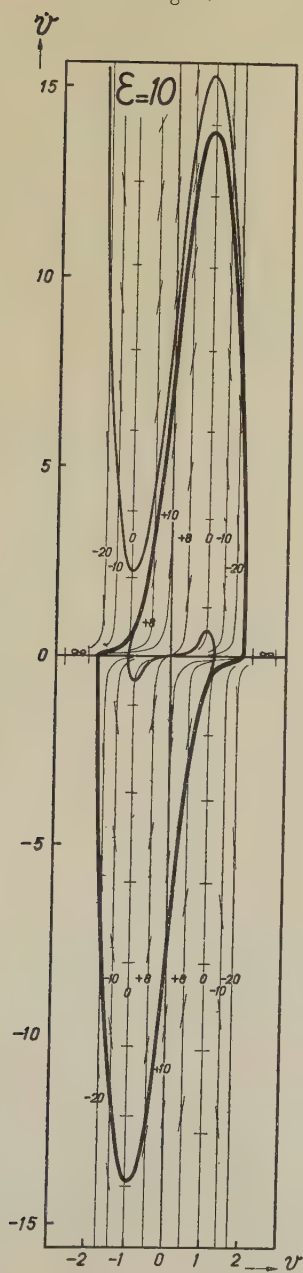
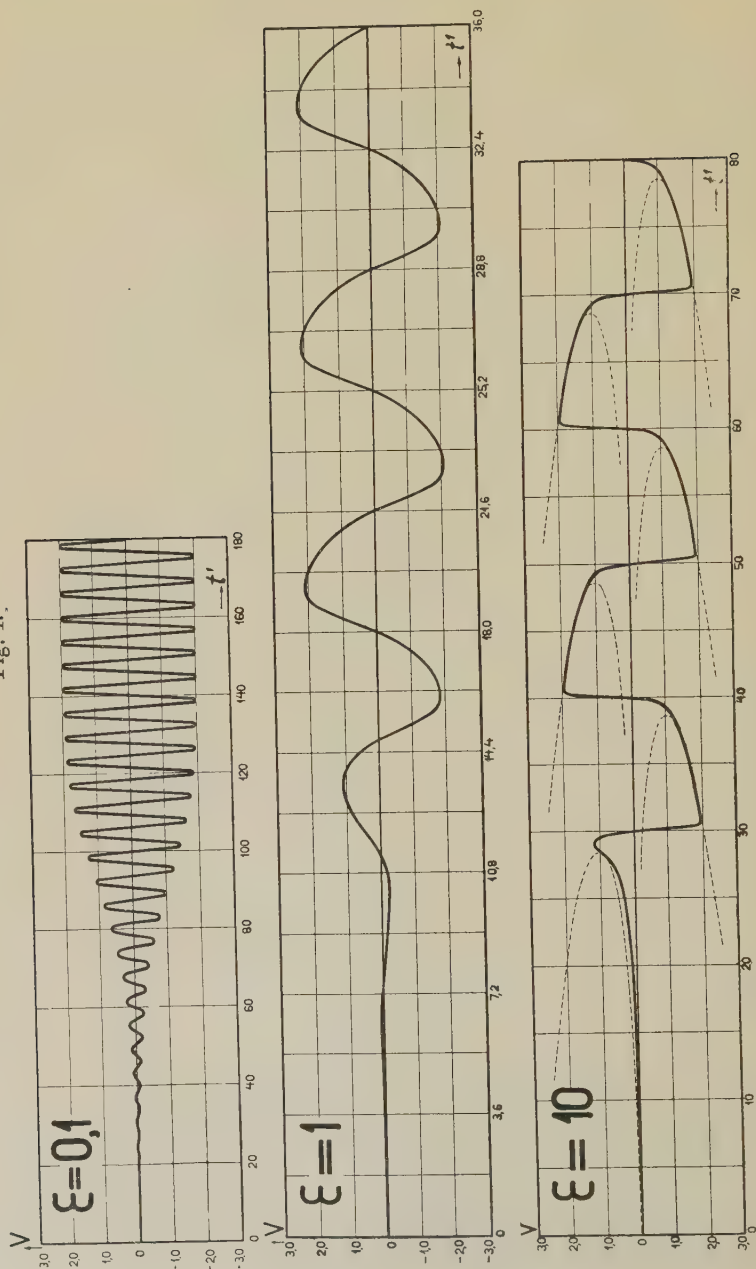


Fig. 4.



only one period practically reaches the final steady state. This steady state is characterized by a very marked departure from the sinusoidal form. It is seen that the amplitude alters very slowly from the value 2 to the value 1 and then very suddenly it drops to the value -2 . Next we observe a very gradual increase from the value -2 to the value -1 and again a sudden jump to the value 2. This cycle term proceeds indefinitely.

Obviously this form of oscillation contains many higher harmonics of considerable amplitude. As will be seen later, the period T , instead of being 2π (as was the case when $\epsilon \leq 1$) increases with increase of ϵ , and when $\epsilon \gg 1$ becomes equal to approximately ϵ itself; that is, we have

$$T \doteq \epsilon.$$

Let us now consider more closely the physical factors determining the value of the period T . If our equation (1) represents the circulation of electricity in a system of resistance R , capacity C , and inductance L , we have, as usual,

$$\alpha = \frac{R}{L},$$

$$\omega^2 = \frac{1}{LC}.$$

Now for the time period expressed in units of t' we have already

$$T \doteq \epsilon,$$

so that, expressed in terms of t , the period becomes

$$T = \frac{\alpha}{\omega^2} = RC, \quad . \quad . \quad . \quad . \quad (13)$$

which is a *time of relaxation* (time constant).

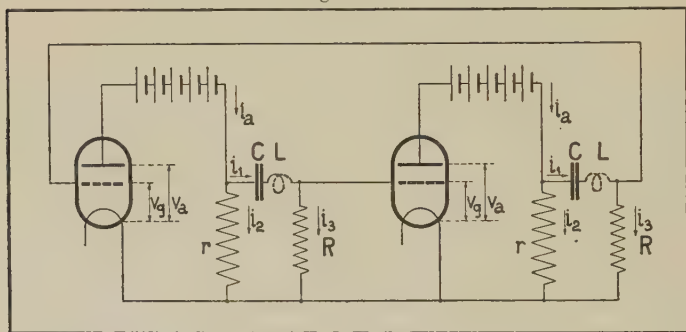
Thus our equation (6) for the quasi-aperiodic case, which differs considerably from the normal approximately sinusoidal solution, has again a purely periodic solution, the time period of which is expressed by the time of relaxation of the system. For this reason the term *relaxation-oscillation* is suggested for this phenomenon.

5. A type of oscillation previously described by Abraham & Bloch* is an example of relaxation-oscillations. These authors used an electrical system comprising two triodes and resistances and capacities only, which system

* Abraham & Bloch, *Ann. de Physique*, xii. p. 237 (1919).

they called "multivibrateur" because of the many higher harmonics of appreciable amplitude which it produced when oscillating. This system, which may be regarded as a two-stage resistance-capacity coupled amplifier with the output coupled back to the input side, is shown in a slightly modified form in fig. 5. In their original description of the system Abraham & Bloch draw attention to the fact that the time period of the oscillations produced by the multivibrator is approximately equal to the product RC (see fig. 5), but, so far as I am aware, no theoretical discussion of the way in which the oscillations are *maintained* has been published.

Fig. 5.



From the symmetrical value of the circuit we may expect that the two triodes can vibrate in exactly opposite phases. It is further known that the potentials and anode currents experience temporal variations closely represented by fig. 4 ($\epsilon=10$). Now, in order to explain the reason for the maintenance of oscillation in this system containing resistances and capacities only, we found it necessary to take into account the inductance L of the wires connected to the two capacities. (These are represented by the dotted lines L in fig. 5.) With the notation of the latter figure the current and potential departures from the unstable equilibrium values are given by the following equation :

$$\left. \begin{aligned} -v_{a1} &= r_1 i_1 = \left(R + L \frac{d}{dt} + \frac{1}{C} \int dt \right) i_3 \\ R i_3 &= -v_{g2} \\ i_{a1} &= i_1 + i_3 = \phi(v_{g1}), \end{aligned} \right\} \dots (14)$$

where $\phi(v_{g1})$ denotes the characteristic of the first triode round the equilibrium position and where, for simplicity,

the influence of the anode potential on the anode current is neglected. Further, assuming that the triodes of this symmetrical system are exactly equal and vibrate in opposite phase, we have

$$v_{g1} = -v_{g2}. \quad (15)$$

From (14) and (15) we derive

$$\left(L \frac{d}{dt} + (R+r) + \frac{1}{C} \int dt \right) v_{g1} = Rr\phi(v_{g1}). \quad (16)$$

Now, as an approximate expression for the characteristic

$$i_{a1} = \phi(v_{g1}),$$

we may take again the third order parabola

$$i_{a1} = S \left(1 - \frac{v_{g1}^2}{v_{g0}^2} \right) v_{g1}, \quad (17)$$

where S is the slope of the anode-current/grid-voltage curve.

Usually the anode lead resistance r is small compared with the grid leak R , i. e.

$$r \ll R,$$

so that from (16) and (17) we have

$$L\ddot{v}_{g1} - R \left\{ (rS-1) - rS \frac{v_{g1}^2}{v_{g0}^2} \right\} \dot{v}_{g1} + \frac{1}{C} v_{g1} = 0. \quad (18)$$

From (18) we note that the "resistance" of the system for small amplitudes is only negative so long as

$$rS > 1,$$

so that we have here the approximate condition for the production of oscillations. If we further make the following substitution :

$$\left. \begin{aligned} t &= t' \sqrt{CL} \\ \frac{v_{g1}}{v_{g0}} &= v \sqrt{\frac{rS-1}{rS}} \\ \epsilon &= R(rS-1) \sqrt{\frac{C}{L}} \end{aligned} \right\}, \quad (19)$$

(18) may be written

$$\ddot{v} - \epsilon(1-v^2)\dot{v} + v = 0, \quad (6)$$

which is the equation originally discussed and which may be said to be the representative differential equation of the multivibrator ($\epsilon \gg 1$). But we may note that, in order to represent the action of the multivibrator by this equation,

we had to take into account the small inductance L of the wires connected to the capacities C , as shown in fig. 5.

We further note from (19) that ϵ depends on the value of $L^{-\frac{1}{2}}$ so that ϵ increases without limit the further L is decreased. We may make a rough estimate of ϵ for the following practical values :

$$R=10^5 \text{ ohms, } rS-1=3, C=0.01 \text{ } \mu\text{fd, } L=10 \text{ cm.}$$

In this case,

$$\epsilon=10^5 \cdot 3 \cdot \sqrt{\frac{10^{-8}}{10^{-8}}}=3 \cdot 10^5,$$

so that the conduction

$$\epsilon \gg 1$$

is certainly satisfied. The smaller the value of the residual inductance L , the greater is this inequality.

It therefore may be concluded that the special vibration of the multivibrator represents an example of a general type of relaxation-oscillations and that in order to explain the maintenance of the oscillations we have to take into account the residual inductance of the system (as shown in fig. 5), however small this may be.

The result of the above discussion illustrates how the form of the solution of differential equations like the representative equal (18) or (6) is entirely altered by taking into account a term with an infinitesimal coefficient (*e. g.* the first term $L\ddot{v}_{g1}$ in (18)).

But the physical reason for taking this into account becomes immediately apparent when we solve (18) or (6) omitting the first term. In this case the solution of (6) is

$$\log v^2 - v^2 = \frac{2t + C}{\epsilon}, \quad . \quad . \quad . \quad . \quad (20)$$

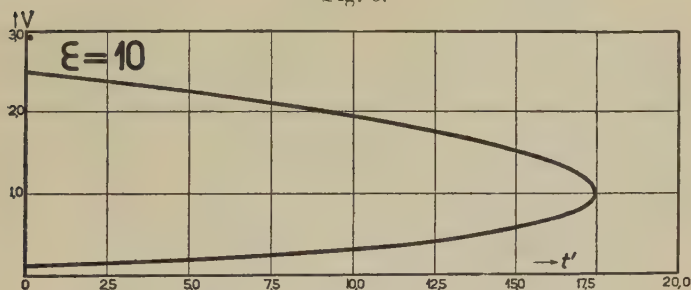
which is represented graphically in fig. 6. We note that the value of v^2 first increases exponentially with time, but near $v^2=1$ the curve bends upwards with an infinite slope, there being further no solution in the real domain. When the inductance is thus disregarded both \dot{v} and \ddot{v} become infinite when $v=\pm 1$, so that the condensers C (fig. 5) would acquire a very large charge in an indefinitely small time. But these infinitely sudden changes of current are prevented by the presence of the small residual inductance.

This is illustrated by the fact that the solution (20) for the derivation of which the inductance has been neglected, and which is represented by the repeated dotted lines in

fig. 4 ($\epsilon=10$), is found to coincide approximately with the exact solution so long as the slope of v is small. Whenever, however, the slope tends to become infinite we note that the term \ddot{v} in (6) becomes of importance and keeping the slope finite maintains the multivibrator in vibration.

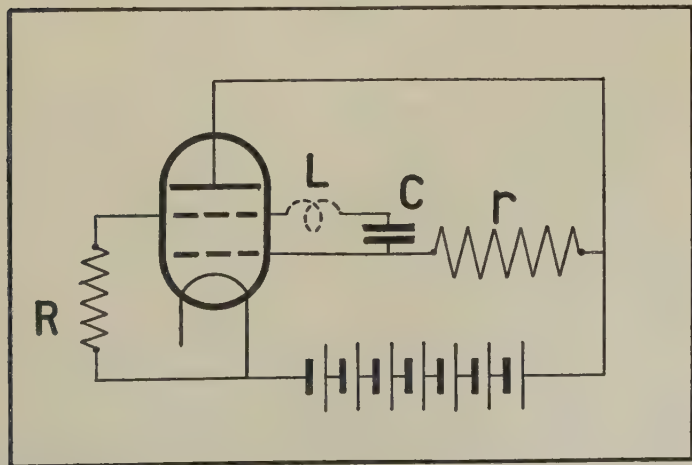
The multivibrator may therefore be compared to a double steam engine with a flywheel which is much too small. The small inertia of the flywheel must, however, be present to carry the system beyond its equilibrium (dead) points.

Fig. 6.



6. Now that the general equation (4) for *relaxation-oscillations* is known, it is an easy matter to devise further electrical systems of the same type. One such a system is

Fig. 7.



depicted in fig. 7 and comprises a tetrode, two resistances r and R , and a condenser C . If we again recognize the

inductance L of the wire connecting the condenser to the outer grid, we find that the circulation of electricity in the system is represented by (6). An experimental test of the system showed that the system produced oscillations with a time period approximately equal to CR . When r is replaced by a telephone receiver the oscillations become audible and the change of frequency by changing R or C is easily demonstrated.

7. Finally it seems quite likely that, when the total characteristic (including the parts with a negative slope) is taken into account, the well-known vibration of a neon-tube connected to a resistance and condenser in shunt* may be similarly treated under the heading of relaxation-oscillations.

Similarly, (though no detailed investigation has been carried out) it is likely that the oscillations of a "Wehnelt" interrupter belong to the general class of relaxation-oscillations and perhaps also heart-beats.

Eindhoven, 6th May, 1926.

Physical Laboratory,
Philips' Glowlampworks, Ltd.

LXXXIX. *The Crystalline Structure of Anhydrite.*

By Prof. JARL A. WASASTJERNA †.

IN a particularly interesting paper published in the July number of this Journal, Messrs. Dickson and Binks examined the structure of Anhydrite. In a note added, it is stated that the present author had previously examined the same problem (*Societas Scientiarum Fennica: Commentationes Physico-Mathematicæ*, ii. p. 26, 1925), and that the two investigations produced structures of the same type but of somewhat different parameter values. From that the conclusion might be drawn, that the two pieces of work stand in certain opposition to each other, if only in detail. But that can hardly be said to be the case.

By virtue of a method of elimination, carried through consistently, which takes every type of structure, mathematically possible, into consideration (in this case there are 85 such different types), the present author has shown that in respect of anhydrite there are two, and only two,

* See, e. g. Schallreuter, 'Ueber Schwingungserscheinungen in Entladungsröhren.' Braunschweig, 1923.

† Communicated by Prof. W. L. Bragg, F.R.S.

possible structures. In the present author's work these structures are denoted as IV and V (pp. 39-40). Let us call them A and B. These two structures are of the same type and extremely closely related to one another. A displacement of the atom groups in the direction of the α -axis of 0.05 transforms one structure to the other.

The atomic coordinates are :—

$$\begin{array}{lcl}
 \text{Ca:} & \left\{ \begin{array}{ll} [[q \cdot \frac{1}{4} \cdot 0]] & [[\bar{q} \cdot \frac{3}{4} \cdot 0]] \\ [[q + \frac{1}{2} \cdot \frac{1}{4} \cdot \frac{1}{2}]] & [[\bar{q} + \frac{1}{2} \cdot \frac{3}{4} \cdot \frac{1}{2}]] \end{array} \right. \\
 \text{S:} & \left\{ \begin{array}{ll} [[r \cdot \frac{1}{4} \cdot 0]] & [[\bar{r} \cdot \frac{3}{4} \cdot 0]] \\ [[r + \frac{1}{2} \cdot \frac{1}{4} \cdot \frac{1}{2}]] & [[\bar{r} + \frac{1}{2} \cdot \frac{3}{4} \cdot \frac{1}{2}]] \end{array} \right. \\
 \text{O:} & \left\{ \begin{array}{ll} [[f \cdot g \cdot 0]] & [[\bar{f} \cdot g + \frac{1}{2} \cdot 0]] \\ [[f \cdot \bar{g} + \frac{1}{2} \cdot 0]] & [[\bar{f} \cdot \bar{g} \cdot 0]] \\ [[f + \frac{1}{2} \cdot g \cdot \frac{1}{2}]] & [[\bar{f} + \frac{1}{2} \cdot g + \frac{1}{2} \cdot \frac{1}{2}]] \\ [[f + \frac{1}{2} \cdot \bar{g} + \frac{1}{2} \cdot \frac{1}{2}]] & [[\bar{f} + \frac{1}{2} \cdot \bar{g} \cdot \frac{1}{2}]] \\ [[h \cdot \frac{1}{4} \cdot k]] & [[\bar{h} \cdot \frac{3}{4} \cdot \bar{k}]] \\ [[h \cdot \frac{1}{4} \cdot \bar{k}]] & [[\bar{h} \cdot \frac{3}{4} \cdot k]] \\ [[h + \frac{1}{2} \cdot \frac{1}{4} \cdot k + \frac{1}{2}]] & [[\bar{h} + \frac{1}{2} \cdot \frac{3}{4} \cdot \bar{k} + \frac{1}{2}]] \\ [[h + \frac{1}{2} \cdot \frac{1}{4} \cdot \bar{k} + \frac{1}{2}]] & [[\bar{h} + \frac{1}{2} \cdot \frac{3}{4} \cdot k + \frac{1}{2}]] \end{array} \right.
 \end{array}$$

We introduce the following new parameters :—

$$\begin{aligned}
 f &= r + t_1 \\
 g &= \frac{1}{4} - u_1 \\
 h &= r - t_2 \\
 k &= u_2.
 \end{aligned}$$

The parameters acquire the following values according to Messrs. Dickson and Binks and to the present author :—

Wasastjerna.	Dickson and Binks*.
$t_1 = 0.16$	$t_1 = 0.15$
$t_2 = 0.16$	$t_2 = 0.15$
$u_1 = 0.19$	$u_1 = 0.18$
$u_2 = 0.19$	$u_2 = 0.18$
$q = \frac{1}{2} + r$	$q = \frac{1}{2} + r$

Alternative A.	Alternative B.
$r = 0.10$	$r = 0.15$

It should be emphasized that r cannot have values in the

* In Messrs. Dickson and Binks' work another system of notation is used. In our calculation the final results have been shortened so that all the parameters are given in two decimals only.

neighbourhood of 0.12–0.13, *i. e.* the value must be either 0.10 or 0.15. There can be no further alternative.

The choice between the alternatives A and B is difficult. While the present author preferred the alternative B, *Dickson and Binks' parameter values show themselves to correspond to the alternative A.* As to the choice between these alternatives the present author does not positively maintain his earlier opinion, which was principally dictated by the fact that the alternative A for the reflexion (210) leads to an intensity, theoretically calculated, which does not satisfactorily agree with experiments. Messrs. Dickson and Binks have found the same difference in the reflexion (210), but nevertheless held to structure A, since structure B, as Mr. Dickson kindly informed the present author, shows defective agreement with the spectrometrically measured reflexions (202), (220), and (440). In the powder photographs examined by the present author, the reflexions (202) and (220) coincide. The reflexion (440) falls outside the ground observed

XC. *On Equilibrium and Motion of a Continuous Medium in Four-dimensional Space.* By D. MEKSYN*.

§ I. *Introduction.*

IN the present paper we apply the laws of four-dimensional space to a continuous medium (see D. Meksyn, *Phil. Mag.* Dec. 1925, p. I227).

Deriving the equation of continuity and the general conditions of equilibrium and motion of such a medium, we accept it as the dynamical laws of an electromagnetic field.

The main results, which are obtained from these considerations, are :—

1. The transformation of mechanical forces in electrodynamics is a particular case of transformation of volume forces in such medium.

2. Radiation of an electron in continuous motion is incompatible with the mechanical equilibrium of the electromagnetic field.

3. In connexion with this we show that a discontinuous change of velocity of a material point (electron) is accompanied by heat generation.

* Communicated by Mr. F. S. Spiers, O.B.E., B.Sc.

I. THE GENERAL LAWS OF EQUILIBRIUM AND OF MOTION.

§ 2. The Law of Continuity.

Take a continuous medium at rest relative to an observer.

The law of continuity of such medium in three-dimensional space is

$$\rho dx dy dz = \text{const.}$$

According to our assumption, motion of the three-dimensional space is equivalent to change of position in four-dimensional space-time continuum. Hence we take as the law of continuity in motion

$$\rho dx dy dz dl = \text{const.}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\text{or} \quad \iiint \rho_1 dx_1 dy_1 dz_1 dl_1 - \iiint \rho dx dy dz dl = 0.$$

Denoting :

$$D = \begin{vmatrix} \frac{\partial x_1}{\partial x}, & \frac{\partial x_1}{\partial y}, & \frac{\partial x_1}{\partial z}, & \frac{\partial x_1}{\partial l} \\ \frac{\partial y_1}{\partial x}, & \frac{\partial y_1}{\partial y}, & \frac{\partial y_1}{\partial z}, & \frac{\partial y_1}{\partial l} \\ \frac{\partial z_1}{\partial x}, & \frac{\partial z_1}{\partial y}, & \frac{\partial z_1}{\partial z}, & \frac{\partial z_1}{\partial l} \\ \frac{\partial l_1}{\partial x}, & \frac{\partial l_1}{\partial y}, & \frac{\partial l_1}{\partial z}, & \frac{\partial l_1}{\partial l} \end{vmatrix}, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

we obtain according to the well-known formula of transformation of coordinates :

$$\rho_1 D = \rho. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

To transform (2), we have

$$x_1 = x + dx = x + \frac{dx}{d\tau} d\tau \dots \dots \quad l_1 = l + \frac{dl}{d\tau} d\tau,$$

$$\text{where} \quad d\tau^2 = dx^2 + dy^2 + dz^2 + dl^2.$$

Denoting :

$$\frac{\partial x}{\partial \tau} = q_x, \quad \frac{\partial y}{\partial \tau} = q_y \dots \quad \frac{\partial l}{\partial \tau} = q_l, \quad . \quad . \quad . \quad (4)$$

we have instead of (2)

$$D = \begin{vmatrix} 1 + \frac{\partial}{\partial x}(q_x d\tau), & \frac{\partial(q_x d\tau)}{\partial y}, & \frac{\partial(q_x d\tau)}{\partial z}, & \frac{\partial(q_x d\tau)}{\partial l} \\ \frac{\partial(q_y d\tau)}{\partial x}, & 1 + \frac{\partial(q_y d\tau)}{\partial y}, & \frac{\partial(q_y d\tau)}{\partial z}, & \frac{\partial(q_y d\tau)}{\partial l} \\ . & . & . & . \\ \frac{\partial(q_l d\tau)}{\partial x}, & \frac{\partial(q_l d\tau)}{\partial y}, & \frac{\partial(q_l d\tau)}{\partial z}, & 1 + \frac{\partial}{\partial l}(q_l d\tau) \end{vmatrix}. \quad (5)$$

Neglecting infinitely small quantities of higher order, we obtain from (3) and (5)

$$\rho_1 \left\{ 1 + \frac{\partial}{\partial x}(q_x d\tau) + \frac{\partial}{\partial y}(q_y d\tau) + \frac{\partial}{\partial z}(q_z d\tau) + \frac{\partial}{\partial l}(q_l d\tau) \right\} = \rho.$$

Hence

$$\begin{aligned} \rho_1 - \rho + \frac{\partial q_x}{\partial x} d\tau + \frac{\partial q_y}{\partial y} d\tau + \frac{\partial q_z}{\partial z} d\tau + \frac{\partial q_l}{\partial l} d\tau \\ + \left\{ \frac{\partial d\tau}{\partial x} q_x + \frac{\partial d\tau}{\partial y} q_y + \frac{\partial d\tau}{\partial z} q_z + \frac{\partial d\tau}{\partial l} q_l \right\} = 0. \quad (6) \end{aligned}$$

The expression in brackets vanishes and (6) becomes after easy transformations :

$$\frac{\partial}{\partial x}(\rho q_x) + \frac{\partial}{\partial y}(\rho q_y) + \frac{\partial}{\partial z}(\rho q_z) + \frac{\partial}{\partial l}(\rho q_l) = 0, \quad (7)$$

the equation of continuity accepted in the Theory of Relativity.

This representation of the law of continuity brings out the meaning of Minkowsky's well-known geometric construction in 'Raum und Zeit,' which has to explain the change of dimensions of bodies (space) in motion.

As we see, it illustrates only the law of continuity of a fluid in motion, and not the properties of space and time.

§ 3. Transformation of Forces.

Consider how volume forces are transformed which arise in a continuous medium and are transmitted by such medium.

Let $F'(X', Y' \dots L')$ be a force on a unit of "mass" (or unit of volume if $\rho = \text{const.}$) of our medium at a system M' and $F(X, Y \dots L)$ the corresponding force in another system M in relative uniform rectilinear motion.

We assume that the force is due to a displacement of the medium.

According to the law of continuity,

$$\rho' F' dx' dy' dz' dl' = \rho F dx dy dz dl,$$

or for the summary forces :

$$\rho' F' dx' dy' dz' = \mathbf{K}' \quad \text{and} \quad \rho F dx dy dz = \mathbf{K},$$

we obtain

$$\mathbf{K}' \frac{dt'}{dt} = \mathbf{K} \quad \text{or} \quad \mathbf{K}' \sqrt{1 - v^2} = \mathbf{K}. \quad (8)$$

We see that the force is transformed not as a vector, but gets an additional factor, which is the result of the law of continuity of the medium.

This explains the somewhat uncommon transformation of mechanical forces in electrodynamics.

§ 4. Statics.

On each element of a continuous medium volume and surface forces can act. At the basis of statics, as in the classical mechanics, we equate to zero the sum of projections of all forces upon the four axes, and the sum of momenta upon six coordinate planes; in all ten equations:

As Epstein has shown (*Ann. d. Phys.* 1911, p. 36) in case of a stationary system we derive from the six equations of momenta the six equations of equilibrium of classical mechanics.

Hence the conditions of equilibrium are

$$\Sigma \mathbf{K}' = 0, \quad \Sigma [r' \mathbf{K}'] = 0. \quad . \quad . \quad . \quad (9)$$

If this system is set in motion, the forces considered from a stationary system become

$$\mathbf{K} = \sqrt{1-v^2} \mathbf{K}',$$

and the "lengths" $r = r'.$

$$\text{Hence} \quad \Sigma \mathbf{K} = \sqrt{1-v^2} \Sigma \mathbf{K}' = 0,$$

$$\Sigma [r \mathbf{K}] = \sqrt{1-v^2} \Sigma [r' \mathbf{K}'] = 0,$$

or if the medium is in equilibrium in one system of reference it remains in equilibrium in every other in relative uniform rectilinear motion.

§ 5. Let ρ be the "density" of the medium. The conditions of equilibrium are the following ten equations:

$$\left. \begin{aligned} & \iiint \rho X dv + \iint T_x d\sigma = 0, \\ & \dots \dots \dots \\ & \iiint \rho (yZ - zY) dv + \iint (yT_z - zT_y) d\sigma = 0, \\ & \dots \dots \dots \end{aligned} \right\} \quad (10)$$

where X, Y, Z, L ; T_x, T_y, T_z, T_L are respectively volume and surface forces, dv and $d\sigma$ are elements of four-dimensional volume and three-dimensional surface.

Using the same method as the classical mechanics, that is, considering the equilibrium of an elementary pentahedron in

998 Mr. D. Meksyn on *Equilibrium and Motion of*
four-dimensional space, and denoting

$$T = \begin{vmatrix} T_{xx} & T_{xy} & T_{xz} & T_{xl} \\ T_{yx} & T_{yy} & T_{yz} & T_{yl} \\ T_{zx} & T_{zy} & T_{zz} & T_{zl} \\ T_{lx} & T_{ly} & T_{lz} & T_{ll} \end{vmatrix}, \quad . . . \quad (11)$$

we obtain :

$$\left. \begin{aligned} T_x &= T_{xx} \cos \alpha + T_{xy} \cos \beta + T_{xz} \cos \gamma + T_{xl} \cos \delta, \\ . & \end{aligned} \right\} \quad (12)$$

where $\cos \alpha = \frac{dx}{d\tau}, \quad \cos \beta = \frac{dy}{d\tau} \dots,$

and $d\tau^2 = dx^2 + dy^2 + dz^2 + dl^2.$

Inserting (12) in the first four equations of (10), and transforming, according to Gauss' theorem, the surface integrals into volume, we obtain the four equations of equilibrium :

$$\left. \begin{aligned} \rho X + \frac{\partial T_{xx}}{\partial x} + \frac{\partial T_{xy}}{\partial y} + \frac{\partial T_{xz}}{\partial z} + \frac{\partial T_{xl}}{\partial l} &= 0, \\ \rho Y + \frac{\partial T_{yx}}{\partial x} + \frac{\partial T_{yy}}{\partial y} + \frac{\partial T_{yz}}{\partial z} + \frac{\partial T_{yl}}{\partial l} &= 0, \\ . & \\ \rho L + \frac{\partial T_{lx}}{\partial x} + \frac{\partial T_{ly}}{\partial y} + \frac{\partial T_{lz}}{\partial z} + \frac{\partial T_{ll}}{\partial l} &= 0. \end{aligned} \right\} \quad . . \quad (13)$$

Inserting (12) in the six equations of momenta (10), transforming again the surface integrals into volume integrals, and using (13), six conditions of equilibrium are derived :

$$T_{xy} = T_{yx}, \quad T_{xz} = T_{zx}, \quad \quad (14)$$

that is, the tensor T is symmetrical.

If we introduce the real axis of time and denote c the velocity of light propagation, we obtain for T the following expression :

$$T = \begin{vmatrix} T_{xx} & T_{xy} & T_{xz} & \frac{iS_x t}{c} \\ T_{yx} & T_{yy} & T_{yz} & \frac{iS_y t}{c} \\ T_{zx} & T_{zy} & T_{zz} & \frac{iS_z t}{c} \\ \frac{iS_{tx}}{c} & \frac{iS_{ty}}{c} & \frac{iS_{tz}}{c} & -W \end{vmatrix} \quad (15)$$

field itself, hence the dynamics of the electron must be based not upon any assumption about the form, sizes, and other properties of the electron, but mainly from the dynamical laws of the electromagnetic field itself.

The considerations of the previous chapter suggest the application to the electromagnetic space, whether there exists a field or not, of the general conditions of equilibrium and motion of a continuous medium (13) (16).

According to electrodynamics the tensor T has the value :

$$\left. \begin{aligned} T_{xx} &= \frac{1}{8\pi} (X^2 - Y^2 - Z^2 + \alpha^2 - \beta^2 - \gamma^2), \\ T_{xy} &= \frac{1}{4\pi} (XY + \alpha\beta), \\ S_{xt} &= \frac{c(Y_\gamma - Z_\beta)}{4\pi}, \\ W &= \frac{1}{8\pi} (X^2 + Y^2 + Z^2 + \alpha^2 + \beta^2 + \gamma^2) \end{aligned} \right\} \dots (17)$$

where X, Y, Z is the electric, and α, β, γ the magnetic forces.

§ 8. *Radiation.*

Let us find what form of solutions of Maxwell's equations is compatible with our general laws of equilibrium.

Let the solution be composed of terms $\frac{f}{r^n}$, where f is a function finite over the whole field; then T will consist of terms $\frac{f_1}{r^{2n}}$.

Now, if we integrate the equations of equilibrium over the whole field, we find that if $n \geq 1$ the resultant stress will be finite, but the electromagnetic momentum and energy infinite unless n is equal to or more than $\frac{3}{2}$ both for the electric and magnetic field. But in this case the Poynting vector $\int \text{div} S \, dv$ taken over the whole field vanishes, or there will be no radiation.

Hence we come to the conclusion that radiation by an electron in continuous motion is incompatible with the mechanical equilibrium of the electromagnetic field.

Radiation can go on only by discontinuous short pulses. These results agree with N. Bohr's model of the atom.

§ 9. Motion.

We apply the general laws of motion (16) to the field. Integrating over the volume of the electron and the electromagnetic space we find :

$$\left. \begin{aligned} m \frac{d}{d\tau} \frac{dx}{d\tau} &= F_x - \int \operatorname{div} T_x dv - \frac{1}{c^2} \int \frac{dS_{tx}}{dt} dv, \\ m \frac{d}{d\tau} \frac{dy}{d\tau} &= F_y - \int \operatorname{div} T_y dv - \frac{1}{c^2} \int \frac{dS_{ty}}{dt} dv, \\ &\dots \dots \dots \\ mc \frac{d}{d\tau} \frac{dt}{d\tau} &= F_t - \frac{1}{c} \int \operatorname{div} S_t dv - \frac{1}{c} \int \frac{dW}{dt} dv. \end{aligned} \right\} \dots (18)$$

where $d\tau = \sqrt{1 - \frac{q^2}{c^2}} dt$; and F_x, F_y, F_t is the external force

$$e \left(E + \left[\frac{q}{c} H \right] \right), \quad \frac{(qF)}{c};$$

the tensor T relates to the field of the electron, therefore we have taken the negative sign.

Now, as according to § 8 all $\operatorname{div} T$ vanish, we obtain from (18) the laws of motion of the electron in the electrodynamics.

§ 10. The Law of Energy.

It is accepted in the electrodynamics to look on the time projection of the conditions of equilibrium as the law of energy; but this is only an equation of motion of the same kind as the first three. On the other hand, the law of energy of a material point represents an invariant property of the four-dimensional space, therefore we must in this case look also for a similar law.

We multiply our equations (18) with $dx, dy, dz, -cdt$ respectively and add them :

$$(Fq) - F_t c - \left(\frac{q}{c^2} \int \frac{d}{dt} S_t dv \right) + \int \frac{dW}{dt} dv = 0, \quad (19)$$

where F is the space part of the four-force, and q the velocity.

As

$$F_t c - \frac{dW}{dt} = mc^2 \frac{d}{dt} \frac{1}{\sqrt{1 - \frac{q^2}{c^2}}},$$

we obtain from (19)

$$(Fq) = \frac{d}{dt} \frac{mc^2}{\sqrt{1 - \frac{q^2}{c^2}}} + \left(\frac{q}{c^2} \int \frac{dS_t}{dt} dv \right), \quad . \quad . \quad (20)$$

or the work done by the external forces is spent on the increase of the kinetic energy of the electron and overcoming the electromagnetic resistance of the field.

If the motion is accompanied by heat generation, then, as we shall see later, the left side of (19) is equal not to zero but to $-R$, when R is the heat absorbed by the electron.

Hence the generalized law of energy will be

$$(Fq) + R = \frac{d}{dt} \frac{mc^2}{\sqrt{1 - \frac{v^2}{c^2}}} + \left(\frac{q}{c^2} \int \frac{dS_t}{dt} dv \right), \quad . \quad (21)$$

or to the work of the external forces is added also the absorbed heat.

The expression (20) of the law of energy, where there is no heat generation, is an invariant of the four-dimensional space; the left side being zero in all systems of reference. But in case of radiation the law (21) will not be invariant; to have such law we must multiply the equations of motion (16) by $dx dy dz dt$, integrate over four-dimensional volume and take the change of energy for an element of track. It is easily seen that this invariant law of energy has the dimensions of action.

It may, perhaps, explain why Planck's universal constant of radiation has also the dimensions of action.

If we insert in (19) for the electric momentum and energy the values given by Theory of Relativity (see M. Laue, 'Die Relativitätstheorie,' p. 134, 1921), and remember that

$$(Fq) - F_t c = 0,$$

we obtain

$$\begin{aligned} \left(\frac{q}{c^2} \int \frac{dS_t}{dt} dv \right) - \left\{ \frac{dW}{dt} dv = q \frac{d}{dt} \frac{4}{3} \frac{q}{c^2 \sqrt{1 - \frac{q^2}{c^2}}} E_0 \right. \\ \left. - \frac{d}{dt} \frac{c^2 + \frac{1}{3} q^2}{c^2 \sqrt{1 - \frac{q^2}{c^2}}} E_0 = \frac{d}{dt} \frac{\sqrt{1 - \frac{q^2}{c^2}}}{3} E_0 \right\} \quad (22) \end{aligned}$$

(*ibid.* p. 226), or if q is not constant, the law of energy is not satisfied.

This contradiction arises because the Lorentz transformations and our law of motion for the electromagnetic field can be considered as valid for variable velocities only to the first approximation.

III. THE DYNAMICS OF A MATERIAL POINT.

§ 11. We apply the four-dimensional dynamics to one particular instance: to a material point moving with heat generation. In this case the fourth law of motion is not a sequel of the first three, the time projection of force can have an arbitrary value, and in order to describe the motion we must use all four equations.

§ 12. *The Law of Energy.*

We have seen that the force is normal to the track. If we denote the scalar product of the force and the track ($Fd\tau$) as the four-dimensional work, we can say that in case of motion without heat effect the work

$$(Fd\tau)=0. \quad . \quad . \quad . \quad . \quad . \quad (23)$$

But in the general case, where heat is absorbed or emitted, the force is not normal to the track, and the work does not vanish; it is equal to

$$(Fd\tau)=Xdx+Ydy+Zdz-Lcdt=-dR, \quad . \quad (24)$$

where the right side represents the heat absorbed by the moving body (if $dR>0$).

This expression is the most general law of energy for a material point.

In so far as the analytical expression (24) is concerned, it can be applied not only to an electron but to a finite piece of matter, but the physical phenomenon is different in these cases.

1. We consider an electron. We have from (24)

$$Xdx+Ydy+Zdz+dR=Lcdt, \quad . \quad . \quad . \quad (25)$$

which expresses that the work of the external forces and the absorbed heat is equal to the increase of the time (or kinetic) energy.

Now the energy of an electron (or proton), as its charge is constant, can be increased only if its velocity increases; hence the absorption (emission) of heat is accompanied by increase (decrease) of its velocity.

2. Quite different appears this phenomenon in a material body. Its time energy consists of the energy of its motion as a whole, and the energy of the electrons and protons.

Absorption by a material body goes on through its

electrons and protons, it increases their energy (or the temperature of the body) but leaves unchanged the velocity of the body as a whole.

These considerations have a bearing on the kinetic theory of matter.

§ 13. *Impulsive Forces.*

Now there arises the question: How can a motion be physically realized, where the force is inclined to the track?

A straight answer gives us the geometry of motion. If the track is discontinuous, the radius of curvature has two directions, and, hence, is not normal to the track at the singular point.

This case corresponds to impulsive forces in dynamics.

§ 14. *Elastic Forces.*

Let us have a material body at rest. We apply to it some impulsive force, and it acquires a velocity v . If $X\Delta t$ is the impulse, then $mv = X\Delta t$. The acquired kinetic energy is $\frac{mv^2}{2}$, the work done by the impulsive force is

$$X\Delta t \cdot \frac{v}{2} = \frac{mv^2}{2},$$

or equal to the acquired kinetic energy. The whole impulse is spent on increase of velocity.

We consider now this problem from the point of view of the four-dimensional dynamics.

The equations of motion are:

$$\left. \begin{aligned} m \frac{d}{d\tau} \frac{dx}{d\tau} &= X, \\ m \frac{d}{d\tau} \frac{dl}{d\tau} &= L, \end{aligned} \right\} \cdot \cdot \cdot \cdot \cdot \quad (26)$$

where $d\tau^2 = dx^2 + dl^2$.

To integrate (26) we denote:

$$\frac{dx}{d\tau} = \sin \phi, \quad \frac{dl}{d\tau} = \cos \phi, \quad \cdot \cdot \cdot \cdot \quad (27)$$

and as $\frac{d}{d\tau} = \cos \phi \frac{d}{dl}$, (26) become

$$\left. \begin{aligned} m \frac{d}{dl} \left(\frac{\cos \phi \sin \phi + \phi}{2} \right) &= X, \\ m \frac{d}{dl} \cos^2 \phi &= L, \end{aligned} \right\} \cdot \cdot \cdot \quad (28)$$

or introducing the real time, and denoting c the velocity of light, we obtain

$$\left. \begin{aligned} -icm \frac{d}{dt} \left(\frac{\cos \phi \sin \phi + \phi}{2} \right) &= X, \\ \frac{mc}{2} \frac{d}{dt} \cos^2 \phi &= L, \end{aligned} \right\} \dots \quad (29)$$

where

$$\sin \phi = \frac{\frac{v}{c}}{\sqrt{1 - \frac{v^2}{c^2}}}; \quad \cos \phi = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}}.$$

Applying (29) to our case, we have

$$\left. \begin{aligned} -icm \left[\frac{\cos \phi \sin \phi + \phi}{2} \right]_0^v &= X \Delta t, \\ \frac{mc}{2} [\cos^2 \phi - 1]_0^v &= L \Delta t. \end{aligned} \right\} \dots \quad (30)$$

We write the equation of energy. For this purpose we multiply the first of (30), as $v = -ic \cos \phi \sin \phi$, with

$$v_1 = -ic \sin \frac{\phi}{2} \cos \frac{\phi}{2},$$

the second with $-c$, and add them :

$$\begin{aligned} R = Xv_1 \Delta t - Lc \Delta t &= -mc^2 \left(\frac{\cos \phi \sin \phi + \phi}{2} \right) \frac{\sin \phi}{2} \\ &\quad - \frac{mc^2}{2} (\cos^2 \phi - 1), \quad \dots \quad (31) \end{aligned}$$

and it is easily seen that this expression will not be equal to zero.

For small velocities

$$R = \frac{mv^4}{12c^2}, \quad \dots \quad (32)$$

or the work is greater than the increase of the kinetic energy ; the difference R is lost by radiation.

If we consider a more general case, where the initial velocity v_1 is changed by impulsive force into v_2 , we find that the heat effect is

$$\frac{m}{12c^2} (v_2 + v_1)^3 (v_2 - v_1), \quad \dots \quad (33)$$

or if $v_2 > v_1$ there is radiation of $v_2 < v_1$ —absorption.

§ 15. *Elastic Collisions.*

Let us have two material points moving with velocities v_1 and v_2 respectively. They collide. What effect will be produced?

From (29) we have

$$\left. \begin{aligned} -icm_1 \frac{d}{dt} \left(\frac{\cos \phi_1 \sin \phi_1 + \phi_1}{2} \right) \\ -icm_2 \frac{d}{dt} \left(\frac{\cos \phi_2 \sin \phi_2 + \phi_2}{2} \right) = X_1 + X_2 = 0, \\ \frac{m_1 c}{2} \frac{d}{dt} \cos^2 \phi_1 + \frac{m_2 c}{2} \frac{d}{dt} \cos^2 \phi_2 = L_1 + L_2 = 0. \end{aligned} \right\} \quad (34)$$

Hence if ϕ_1' and ϕ_2' are the corresponding angles after collision we have from (34)

$$\left. \begin{aligned} m_1 \cos \phi_1 \sin \phi_1 + m_1 \phi_1 + m_2 \cos \phi_2 \sin \phi_2 + m_2 \phi_2 \\ = m_1 \cos \phi_1' \sin \phi_1' + m_1 \phi_1' + m_2 \cos \phi_2' \sin \phi_2' + m_2 \phi_2', \\ m_1 \cos^2 \phi_1 + m_2 \cos^2 \phi_2 = m_1 \cos^2 \phi_1' + m_2 \cos^2 \phi_2', \end{aligned} \right\} \quad (35)$$

two transcendental equations, which define the motion after collision.

For small velocities (35) becomes the well-known conditions of elastic collision in classical mechanics.

The energy lost or gained by radiation during the collision is from (33), (35),

$$\frac{4}{3} \frac{m_1 m_2}{c^2} \frac{(m_1 v_1 + m_2 v_2)^3}{(m_1 + m_2)^4} (v_2 - v_1), \quad . \quad . \quad . \quad (36)$$

or the heat effect is equal and opposite in the two material points.

§ 16. *Heat.*

This analysis elucidates some of the laws of matter.

1. Heat is not a result of continuous motion of molecules. A material point in continuous motion does not generate heat, and there is no reason why a great number of them should produce this effect. Heat generation arises solely from discontinuous motion.

At the absolute zero only continuous motion is possible.

2. If electrons and protons (a gas) are enclosed in a vessel, so that no heat interchange is possible with the outer space, once brought in motion, they will indefinitely continue it.

This does not apply to finite pieces of matter, which, as we have seen (§ 12), would soon stop.

XCI. *The X-Ray Spectra of the Lower Elements.*

By ROBERT THORÆUS*.

[Plates XVII. & XVIII.]

PART II.

IN connexion with the recently published wave-length measurements within the K- and L-series of the lower elements† some observations have been made concerning the structure and general appearance of these X-ray spectra. Some new wave-lengths have also been measured.

When studying the earlier wave-length tables of the lower L-series it was found that the main lines α and β_1 are accompanied by only one satellite called α_3 . By using the new high-vacuum spectrograph with a gypsum crystal that gives a rather good dispersion within this range of wave-lengths, both the main lines have been proved to be more complicated. As far as can now be stated, they have two satellites each that have been measured for the elements Br (35) to Cu (29). Prof. M. Siegbahn has proposed to denote these four satellites α' , α'' , β' , and β'' . When doing this it must, however, be pointed out that the line called α' , as far as can be stated from the wave-lengths, may be the same one as the earlier α_3 line. The intensity of the satellites on the plates is rather good. When passing from Zn (30) to Cu (29) a very interesting case appears. The satellites of Zn are rather well-defined and relatively strong, but in the case of Cu and still more that of Ni (28) they are very diffuse and tend to disappear in the continuous blackening on the photographic plate. Owing to this, it has not been possible to measure them for elements below Ni (28).

The L-series of Ge (32) lie just within the range of elements investigated here, but they have never before been completely measured, as this element and its compounds are very rare. By friendly help, however, from Dr. L. M. Dennis of Cornell University, U.S.A., I was able to get a small amount of metallic germanium quite sufficient for my exposures. The powdered metal was applied on a scratched aluminium plate dovetailed in the copper anticathode.

In some cases I have also been able to measure the very faint emission lines $\beta_3 \beta_4$. It was not, however, possible to separate them, and so I have given only a mean value.

* Communicated by Prof. Manne Siegbahn, D.Sc.

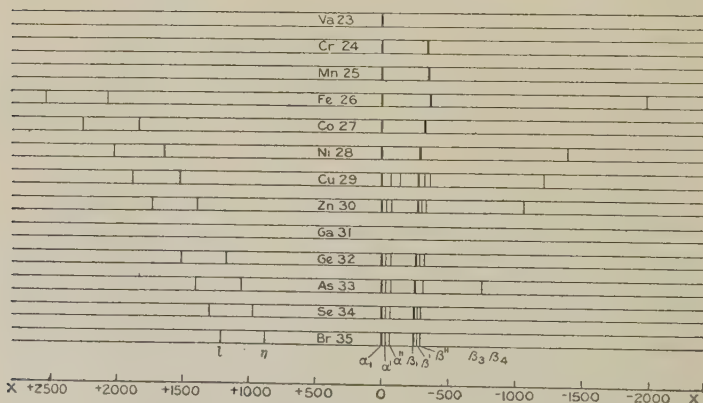
† Phil. Mag. February 1926.

In order to extend the knowledge of the K- and L-series, I have also made some attempts to photograph the K-series of oxygen and the L-series of vanadium with palmitic acid as crystal. In the case of oxygen fine-powdered quartz SiO_2 , was applied on the scratched copper anticathode. After an exposure of about two hours with 35 milliamps and 5000 volts, I found three lines on the photographic plate. For identifying the lines, I had arranged, just before the plate, a cross-wire that left a white shadow on the plate. As the position of this shadow was known, I had no difficulty in identifying one of the lines as $\text{SiK}\alpha$ in the third order, and taking this line as reference the other lines could easily be measured. In the following Table I. I give the calculations.

For taking the L-series of vanadium I have used ferro-vanadium as anticathode substance. This alloy contained about 45 per cent. Va, and was kindly supplied by the Metallographic Institute in Stockholm. The method of identifying the lines was the same as mentioned above. The calculations are to be found in Table II.

In Part I. I gave the wave-lengths of the strongest lines of the lower L-series. In Table III. I have now collected these values together with the new ones, and Tables IV. and V. give the calculated ν/R and $\sqrt{\nu/R}$ values. Comple-

Fig. 1.



mentary to this, I have also drawn the diagram in fig. 1, containing all the up to date known wave-lengths of the lower L-series. Here the $L\alpha$ lines are arranged on a vertical, and the other ones are set up from the scale given in the diagram. It is clearly to be seen how the displacement of

TABLE I.

Plate No.	Line No.	Intensity.	Distance, mm.	Correction, $\Delta\phi$.	ϕ .	λ .	ν/R .	$\sqrt{\nu/R}$.	
T. 246	1	...	Ref.	—	17° 29'	21.33	Si $K\alpha_{III}$.
	2	...	+ 9.3	+ 2° 3'	19° 32'	23.73	38.40	6.197	O $K\alpha$.
	3	...	+ 20.5	+ 4° 38'	22° 1'	26.61	Cu $L\alpha_{II}$.

TABLE II.

Plate No.	Line No.	Intensity.	Distance, mm.	Correction, $\Delta\phi$.	ϕ .	λ .	ν/R .	$\sqrt{\nu/R}$.	
T. 247	Cross-wire.	...	Ref.	—	20° 12'	24.2	37.7	6.13	V α $L\alpha$.
	1	...	-1.7	-0° 16'	19° 56'				

TABLE III.
Wave-length Values of the lower L-Series.

Wave-lengths in Å. U.	Br 35.	Se 34.	As 33.	Ge 32.	Zn 30.	Cu 29.	Ni 28.	Co 27.	Fe 26.	Mn 25.	Cr 24.	Va 23.
λ	9.563	10.271	11.047	11.920	13.95	15.19	16.55	18.20	20.12			
η	9.234	9.939	10.710	11.585	13.61	14.83	16.17	17.77	19.65			
$\alpha_1, 2$	8.357	8.971	9.650	10.414	12.224	13.308	14.528	15.94	17.38	19.39	21.53	24.2
α'	8.326	8.939	9.616	10.378	12.191	13.24						
α''	8.297	8.903	9.581	10.341	12.150	13.172						
β_1	8.108	8.717	9.394	10.152	11.938	13.029	14.235	15.62	17.22	19.04	21.19	
β'	8.086	8.698	9.372	10.131	11.934	12.99						
β''	8.065	8.671	9.346	10.102	11.893	12.96						
β_4 } β_3 }	8.911	...	11.16	12.10	13.14	...	15.61			

some groups of lines increases very much, especially that of the $l\eta$ and $\beta_3\beta_4$ lines. In the case of Fe (26) the distance between the $l\eta$ - and the $\alpha_1\beta_1$ -groups is about 2.5 Å.U., that is more than six times the distance between the lines within each group.

Concerning the $L\alpha$ line something peculiar seems to happen in the range of Zn and Cu. In the case of Zn this line is rather sharp, slightly broader than the slit, but the $L\alpha$ of Cu and still more that of Ni is very broad and diffuse. As this also appears when using a mica crystal, it cannot be simply connected with the increased dispersion, and so I have performed a special investigation concerning the $L\alpha$ lines of Zn, Cu, and Ni in different chemical states. The $L\alpha$ lines have been examined for the following substances:—

1. Zinc: Zn (met.), ZnO, and ZnS.
2. Copper: Cu (met.), Cu₂O, CuO, and CuS.
3. Nickel: Ni (met.), NiS, and Ni₂O₃.

All the compounds were applied on aluminium plates, as mentioned above. The results are rather surprising. In the case of Zn the $L\alpha$ lines are all alike, but for Cu and Ni their general appearance changes very thoroughly. The $L\alpha$ of Cu (met.) and Cu₂O are quite alike, a very broad line with diffuse edges, but for CuO and CuS they consist of *two lines clearly separated* and each of them of about the same breadth as the $L\alpha$ of Zn. Thus the metallic and monovalent Cu behave in the same way, but the bivalent Cu quite differently. In the case of Ni I have found that the metallic and bivalent ones are equal, but the trivalent atom in Ni₂O₃ seems to give a separated $L\alpha$ line, although not so sharply defined. In fig. 2 (Pl. XVII.) I supply the photometer curves of Cu $L\alpha$ from CuO, where the separated lines are clearly to be seen. The curves are taken on three different places of the photographic plate. In fig. 3 (Pl. XVIII.) some photograms of different L-series are collected. All of them are taken with a gypsum crystal.

In Part I. I gave a diagram showing how the wave-length difference $L\alpha - L\beta_1$ runs very smooth down to Zn (30), but for Cu (29) and the following elements belonging to the iron group behaves quite differently. Now the observations concerning the structure and general appearance of the $L\alpha$ line seem to point in the same direction. Down to Zn the structure and intensity of both the $L\alpha$ and the $L\beta_1$ lines are quite regular, but at copper they have suddenly changed very considerably. The $L\alpha$ line is very broad and diffuse, and in

the case of Ni it is most diffuse against longer wave-lengths. The intensity of the $L\beta_1$ is smaller when compared with that of the $L\alpha$, all the satellites are very faint and, moreover, from the diagram fig. 1 it will be seen how they are somewhat displaced. So there are many facts that appear simultaneously in the same range of elements, but it is difficult to say whether they are of the same character or not.

The irregularity of the wave-length difference may refer to some disturbances in the energy levels L_{II} L_{III} probably connected with the magnetic properties of the iron group elements. This suggestion seems to be supported by the observation that the deviation is biggest in the case of iron, and that a similar effect also appears within the K-series of these elements. Now we may also imagine that the above-mentioned sudden change of the structure and intensity within the L-spectra refers to some magnetic disturbances. Further, it may be due, more or less, to some changes of the electronic arrangement in the energy levels M_{IV} M_V that is connected with the electronic building-up process by which, in the range of these elements, the energy levels just mentioned probably get their electronic equipment.

In the case of bivalent Cu the $L\alpha$ line was found to consist of two lines. This may be due to the chemical state of the Cu atom. In recent papers Mr. E. Bäcklin * and Mr. B. B. Ray † have found such changes in the $K\alpha$ line of S (16) when using different compounds. As the $K\alpha_1$ and $K\alpha_2$ lines were quite separated, they got three lines on the photographic plate. In my case the $L\alpha_1$ and $L\alpha_2$ lines are not separated, and so, if due to the same effect, only two lines might be expected.

From the ν/R values of the new wave-lengths some energy-levels can also be determined. The following transitions are then to be considered :--

$$M_I = \begin{cases} L_{II} - L\eta \\ L_{III} - Ll \end{cases}$$

$$M_{II, III} = K_I - K\beta_1$$

$$M_{IV} = L^{II} - L\beta_1$$

$$M_{IV, V} = L_{III} - L\alpha_1.$$

The K- and L-absorption edges of the elements in question are, however, not very accurately measured. Mr. E. Åse, in

* *Zeits. f. Physik*, Bd. xxxiii. Heft 7 (1925).

† *Phil. Mag.* Sept. 1925.

TABLE VI.
 ν/R Values of the Energy Levels

Element No.	K_I .	L_{IV} . $K_I - K\alpha_2$.	L_{III} . $K_I - K\alpha_1$.	M_I .		$M_{II, III}$. $K_I - K\beta_1$.	M_{IV} .	$M_{IV, V}$.
				$L_{II} - L\eta$.	$L_{III} - L\delta$.			
35 Br	992.57	117.69	114.29	18.99	18.99	13.50	5.29	5.19
34 Se	932.02	108.37	105.40	16.67	16.70	11.57	3.87	3.80
33 As	874.01	100.02	97.42	14.92	14.92	10.36	3.02	3.02
30 Zn	711.73 ¹	77.10	75.39	10.10	10.09	6.80	0.90	0.84
29 Cu	661.59 ¹	70.32	68.84	8.82	8.84	5.68	0.38	0.36
28 Ni	614.12 ¹	64.70	63.27	8.30	8.27	5.40	0.70	0.67
27 Co	568.24 ¹	59.04	57.80	7.74	7.70	4.73	0.74	0.60
26 Fe	524.00 ¹	53.44	52.40	7.04	7.10	4.17	0.54	0.60
25 Mn	481.83 ¹	48.18	47.34	—	—	3.70	0.18	0.34
24 Cr	441.23 ¹	43.12	42.40	—	—	3.61	0.12	0.10

¹ These values are kindly supplied by Mr. E. Asce, and belong to the metallic form of the elements.

this laboratory, has recently been working with measurements in this region, and from his not yet published results he has kindly supplied me those of his new values which are necessary for the above calculations—that is, the K-absorption edges of the elements Zn (30)—Cr (24). Because of waiting for these values the publication of this paper has been somewhat delayed in order to get the content as complete as possible.

From the K-levels as measured by Åse I have calculated the values of the L_{II} , L_{III} , and $M_{II, III}$ levels by using Siegbahn and Dolejšek's precision-measurements within the K-series of these elements*. By the above formulas the M_I , M_{IV} , and $M_{IV, V}$ levels are then calculated. In Table VI. I have collected all the energy-levels.

By combining the doublet L_{II} and the levels L_{II} and L_{III} I have obtained two values of the M_I level. As can be seen from the table the agreement is very good. The difference between two corresponding values never amounts to 1 per cent.

The following Table VII. gives the $\sqrt{\nu/R}$ values of the energy-levels as calculated from Table VI.

In the diagram fig. 4 the $\sqrt{\nu/R}$ values of the M-levels are plotted against the atomic number Z . From this diagram it is clearly to be seen how a sudden change in the slope of the curves just appears at Cu (29), thus corresponding to the above-mentioned changes observed in the structure and general appearance of the L-series of these elements.

Somewhat aside from the subject dealt with above, I supply the drawings (Pl. XVII. fig. 5) of a small high-vacuum spectrograph that has proved to be rather convenient for finding the first approximate wave-length value of an unknown X-ray line. For this purpose there are no requirements of accuracy, and so the construction may be kept quite simple. The photograms are taken on circular bent film-strips 162×23 mm. in size and placed at a distance of 85 mm. from the reflecting surface of the crystal. As may be seen from the drawing, a cone is arranged for inserting the film-strip, the position of which is then quite fixed. This arrangement, however, only allows reflecting angles from 0 to about 40° . When this spectrograph is used a rather small dispersion is wanted, that means in general small angles, and the satisfying of this condition raises no difficulties. By choosing a crystal with large lattice-constant a reflecting angle smaller than the above maximum of 40° will easily be obtained. When an unknown X-ray line is to be approximately determined it is

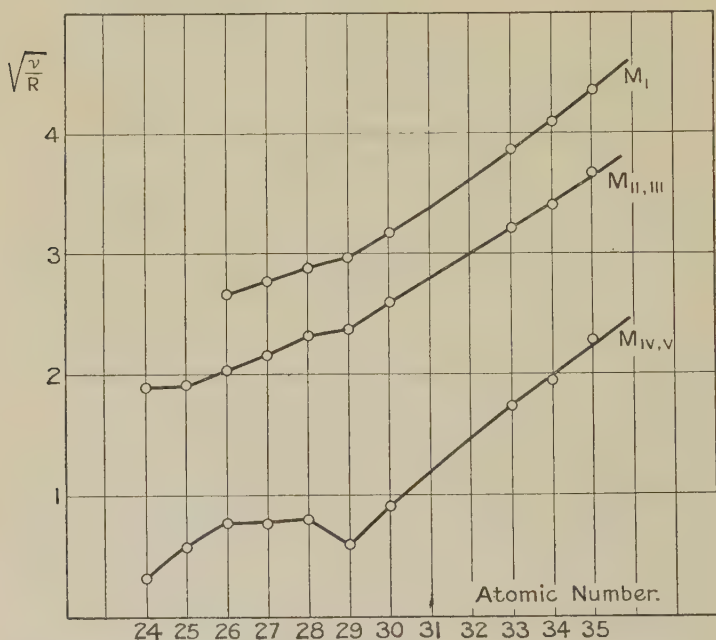
* *Zeits. f. Physik*, Bd. x. Heft 3 (1922).

TABLE VII.
 $\sqrt{\nu}/R$ Values of the Energy Levels.

Element No.	K_I	L_{II}	L_{III}	M_I		$M_{II, III}$	M_{IV}	$M_{IV, V}$
				$L_{II}-L_{II'}$	$L_{III}-L_{II'}$			
35 Br	31.51	10.85	10.69	4.36	4.36	3.67	2.30	2.28
34 Se	30.53	10.41	10.27	4.08	4.09	3.40	1.97	1.95
33 As	29.56	10.01	9.87	3.86	3.86	3.21	1.74	1.74
30 Zn	26.68	8.78	8.68	3.18	3.17	2.61	0.95	0.92
29 Cu	25.72	8.39	8.30	2.97	2.97	2.38	0.62	0.60
28 Ni	24.78	8.04	7.96	2.83	2.88	2.32	0.84	0.82
27 Co	23.84	7.68	7.60	2.78	2.77	2.17	0.86	0.77
26 Fe	22.89	7.31	7.24	2.65	2.66	2.04	0.73	0.77
25 Mn	21.95	6.94	6.88	—	—	1.92	0.42	0.58
24 Cr	21.01	6.57	6.51	—	—	1.90	0.35	0.32

necessary to expose continuously over a rather big range of angle-values, and to run such an exposure within a suitable time requires a good intensity of the X-ray beam. To satisfy this requirement the slit is placed as near the anti-cathode as possible. The slit itself should be at least 0.2 mm. wide.

Fig. 4.



The crystal table is also of a very simple construction that, I think, will easily be seen from the drawing. The body of the spectrograph is built of 5 mm. brass plate and all soldered together. At the circumference of the upper plate is arranged a scale for reading the movement of the crystal. The spectrograph is then connected to the X-ray tube by a cone; this is quite necessary, to get a good tightening on this point. Other details, I think, will easily be understood when looking at the drawing.

In conclusion I wish to express my best thanks to Professor Manne Siegbahn, who has suggested me this work, for his kind interest and much valuable advice on different points during the whole investigation.

Upsala,
Physical Laboratory of the University,
April, 1926.

XCII. *Photophoresis of Colloidal Particles in Aqueous Solutions.* By WILFRED W. BARKAS, M.Sc.*

[Plate XIX.]

SUMMARY.

THE action of light and X-rays on aqueous solutions of copper, gold, silver, and gamboge is observed. The cloud of particles, settling out of suspension under the action of gravity, moves on the average towards the light side of the containing cell, being thus light negative on Ehrenhaft's convention. The upper surface of the cloud takes up a characteristic formation under the action of light, the boundary becoming much more sharply defined. The velocities of drift are calculated for particles near the top of the cloud; these are greater in most cases than the velocities found by Ehrenhaft for particles suspended in gases and illuminated by the intense beam of the ultra-microscope. The change of size of gold particles under the action of light is also measured.

WHILE determining the sizes of colloidal copper particles in aqueous solutions, by the method of observing the rate of fall of the cloud-surface, it was noticed that light had a strong action on the formation of the settling cloud. If the particles settled in the dark, the cloud surface was horizontal and the exact upper boundary indefinite over a vertical distance of about 0.5 mm. The radius given by this method, by Stokes's law, was, for the smallest particles which settled out, in good agreement with that determined by other methods, *e. g.* centrifuging or by the final variation of concentration with depth (Trans. Far. Soc. xxi., i. 1925). If, however, the solution was exposed to light, the cloud moved on the average towards the source of light, and its upper surface became more sharply defined than before.

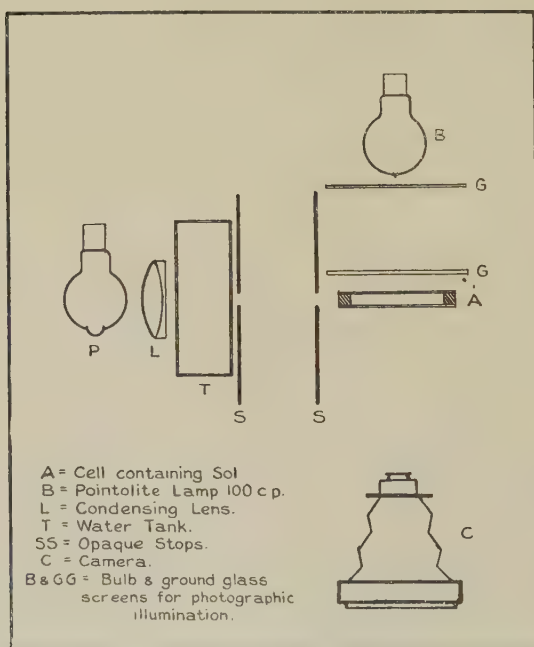
A few preliminary experiments were made which are recorded here, the quantitative measurements being taken from a single set of observations, but qualitatively the results are quite general.

A glass-sided cell A (fig. 1), 7.7 cm. square and 1 cm. thick, was set up vertically containing a suspension of copper particles. The narrow face of the cell was illuminated by light from a 100-c.p. pointolite, P, placed at about 20 cm.

* Communicated by Prof. A. W. Porter, D.Sc., F.R.S.

away, the heat rays being absorbed by a large glass tank, T, 8 cm. thick. Except for the side facing the light, the cell was completely screened from all light rays by the opaque screens S, S. The broad face of the cell could be photographed in the camera, C, by means of transmitted light from a lamp, B, on the axis of the camera lens, diffused through two ground-glass screens G, G, an exposure of 30 seconds being required. This light was, of course, only used during the taking of photographs.

Fig. 1.



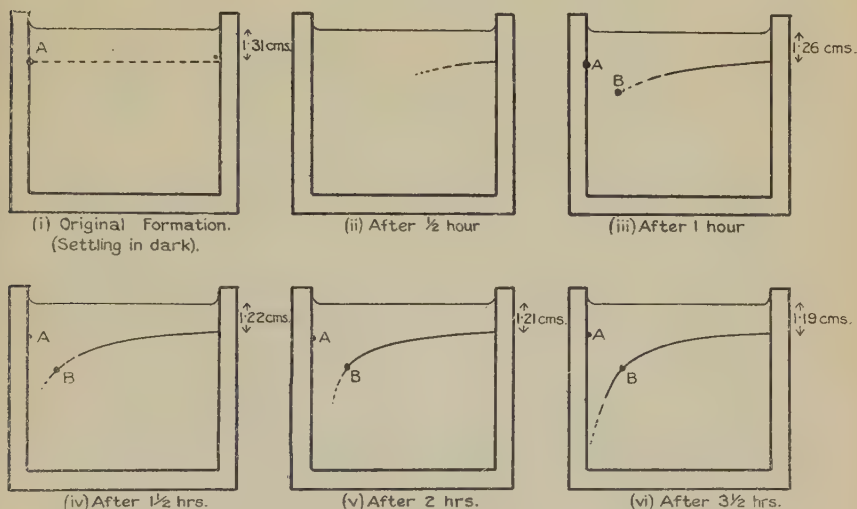
Plan of apparatus for photographing photophoresis of colloidal solutions.

The photographs taken are mostly not good enough for half-tone production, though Plate XIX. gives representative prints corresponding to diagrams in fig. 2, nos. i., iii., and vi. The figures are drawn from the photographs. The curved line represents the upper surface of the cloud; it is shown continuous where the cloud-surface is definite, and dotted

where it is diffuse. The details of the experiment are as follows :—

After settling under gravity in the dark for 18 hours, two parallel diffuse cloud-surfaces can be seen (Pl. XIX., 1) at depths of 1.0 and 1.31 cm., indicating two predominant sizes of particles (3.15 and 3.58×10^{-6} cm. radius). When the activating light was turned on, on the right-hand side, both cloud-surfaces moved similarly to one another. Photographs were taken every half hour. Fig. 2, nos. i. to vi., show the change of formation of the lower of the two clouds only,

Fig. 2.



Light on right-hand side (see Pl. XIX.). (The curved line represents the upper surface of the cloud; a full line representing a sharp, and a dotted line a diffuse boundary.)

up to $3\frac{1}{2}$ hours in the light; after this, further change was very slow. The surface of this cloud became sharply defined on the right and disappeared completely on the extreme left (fig. 2, ii.). It gradually took up the new form, and finally became sharp over its entire length from the top right-hand to the bottom left-hand corner of the cell, the definition being now much sharper than in the original cloud (fig. 2, vi.). It should be noticed that the cloud-surface on the top right-hand side (*i. e.* the edge near the light) rises against gravity a distance of 0.05 cm., *i. e.* at a rate of 1.4×10^{-5} cm./sec. for the first hour, which is about 0.7 times the rate of fall under gravity in the dark.

The movement of the cloud-surface indicates that the whole cloud is drawn over to the light side of the cell until equilibrium is set up; this equilibrium presumably being reached when the forces due to the light balance the osmotic pressure of the solution. If this is the case, we may obtain some idea of the speed of drift of the particles by considering, for example, a particle originally situated in the top left-hand corner of the cell in fig. 2 (at the point A in no. i.). If we make no assumption as to the direction of drift, it must move *at least* as far as to the nearest point on the cloud-surface (to the point B in nos. iii. to vi.). From the times taken this involves a minimum velocity of 5×10^{-4} cm./sec. for the first hour, or 1.6×10^{-4} cm./sec. for the whole period of $3\frac{1}{2}$ hours. In the first hour this is 25 times the rate of fall under gravity in the dark. If we assume only horizontal drift (*i. e.* along the beam of light), the velocity of such a particle cannot be so definitely calculated, but it will be of the same order. For points lower down in the suspension the motion is in both cases smaller, though not in general zero.

This same suspension is afterwards left undisturbed in the dark for 17 hours. The top of the cloud is now roughly horizontal again, but very diffuse except for the edge previously nearest the light, which is still as sharp as before, but which in the case shown in the diagram has fallen to 1.35 cm. below the liquid surface, this velocity being 2.6×10^{-6} cm./sec., or only 0.13 that of the previous night.

After the cloud had been built up on the right as previously described, fig. 3 shows the effect of changing the light over to the left-hand side of the cell. A complete reversal of the cloud formation takes place in 40 minutes. For a particle originally at the point A (fig. 3, i.) this involves a least possible velocity of 1.25×10^{-3} cm./sec.

These velocities for the particular suspension under consideration may be summarized as follows:—

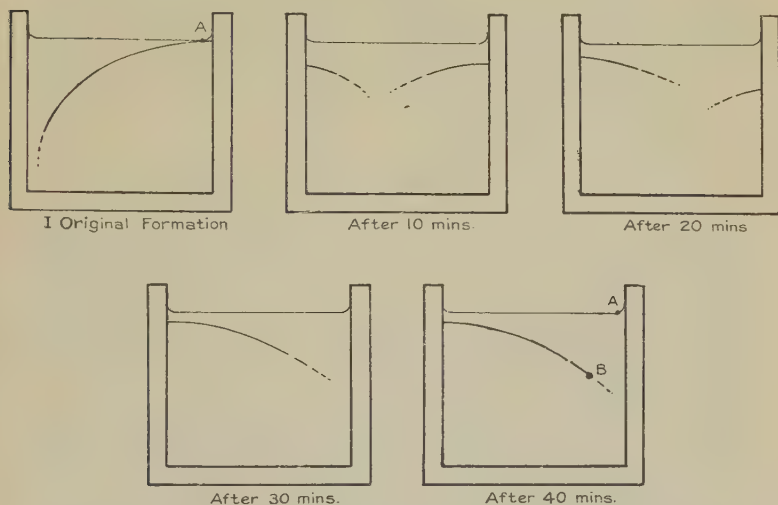
Fall of cloud under gravity	2.02×10^{-5} cm./sec.
Particles at point A (fig. 2) on exposure to light	} for 1st hour 5.0×10^{-4} cm./sec. } average of $3\frac{1}{2}$ hours 1.64×10^{-4} cm./sec.
Particles at A (fig. 3) on reversing direction of light ..	
	} average for $3\frac{1}{2}$ hours 1.25×10^{-3} cm./sec.

In later experiments the beam of light was rendered parallel by the introduction of the lens L (fig. 1), but this made no apparent difference to the cloud formation.

If the suspension is illuminated as soon as it is set up, without giving time for the particles to settle down in the

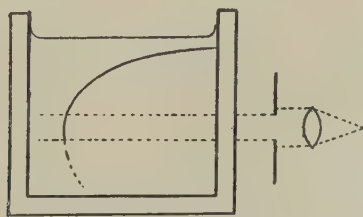
liquid, the reduction of volume of the cloud under the action of light is not measurably different from what it would have been if the cloud had settled for the same time under the action of gravity alone. Again, in the case of solution which had been left to stand for several weeks until it contained in suspension only those particles which remained permanently suspended by brownian movement (*i. e.* in which there was

Fig. 3.



Change of cloud-formation on changing light from right- to left-hand side.

Fig. 4.



Cloud formation due to a narrow parallel beam of light

no surface to the cloud of particles within the body of the solution), no cloud-surface was formed upon exposure to light. That this suspension was still rich in particles was confirmed by observation under the microscope. In the case illustrated in fig. 2, however, where settling had previously taken place, the volume of the cloud after

3½ hours was about 10 per cent. smaller than it would have been, in the same time, if acted on by gravity alone.

The next trial was made by illuminating the side of the cell by an accurately parallel beam of light from an arc lamp along the narrow parallel path shown by the dotted lines in fig. 4. In this case the cloud is drawn in at the bottom as well as at the top, the greatest horizontal width being in the beam of light. The cloud again becomes sharply defined, first at the top right-hand corner of the cell, though this is now well outside the direct illumination of the beam of light, and again this portion rises slightly against gravity.

These experiments were repeated with colloidal suspensions of gold, silver, and gamboge, the effects being in each case the same.

X-Rays.

A suspension of gold was exposed to a narrow penetrating beam of X-rays from a tungsten anti-cathode. In this case also the cloud drifted towards the source of X-rays, the formation being similar to that shown in fig. 4. It is not possible to compare the intensities of the X-rays and light used, but the time taken to build up the cloud was roughly the same in each case.

It cannot be assumed that the observed changes in cloud formation are due entirely to the action of light without other disturbances, such as temperature changes in the solution or slight convection currents to which the cloud would be very sensitive; and for this reason no attempt is here made to deduce a mathematical expression for the shape of the cloud-surface. It seems, however, that the light exerts a force on the particles, causing them to move towards the source of light, the greatest movements taking place nearest the top of the cloud where the concentration is least, in accordance with the laws of distribution of colloidal particles.

Change of Size of Gold Particles.

It was noticed that the colour of the gold suspension changed from ruby-red to deep mauve as a result of exposure to light, but that no such colour-change took place after exposure to X-rays. In one instance the change of colour along the narrow beam of light (as in fig. 4) could be seen quite distinctly, and remained visible for about an hour after the light had been turned off. The suspension previously exposed to X-rays changed colour on subsequent exposure to ordinary light.

Three samples of gold solution were taken from the same stock, one having been exposed to light, one to X-rays, and one having been kept in the dark. These were set up in hard glass test-tubes and allowed to settle in the dark for twelve days. The transition of colour from clear liquid at the top of the tube to dense solution below was indefinite over a depth of about 6 mm., showing that particles of all sizes were present (even after exposure to light); but the mean position of the cloud-surface was taken from the sixth to the twelfth day. This gave the mean size of gold particles in the solution as follows:—

	Radius.	Velocity.
Particles kept in the dark	2.3×10^{-6} cm.	0.176 cm./day.
Particles exposed to X-rays	2.3×10^{-6} „	0.176 „
Particles exposed to light	2.9×10^{-6} „	0.272 „

These show a decided increase in size after exposure to light.

Ehrenhaft (*Ann. der Phys.* 1918, p. 81) describes experiments showing the drift of particles suspended in gases, to which phenomenon he ascribes the name photophoresis. In several respects, however, the above results are not entirely analogous. In his experiments he deals with individual particles in gases which drift directly parallel to the beam of light except for the gravity component. In air certain particles drift in the direction of the light-beam, *e. g.* gold and silver. These he terms light-positive. Others drift against the direction of the light (light-negative). In the present experiments the particles of gold and silver, as well as copper and gamboge, are light-negative. Again, in the very intense beam of the ultra-microscope, Ehrenhaft's velocities of drift in air are some five or ten times greater than the velocities of fall under gravity in the same medium, the velocity being proportional to the intensity of the light. The actual velocities he records are of the order of 10^{-4} cm./sec. This ratio of velocities is less than half that in the present experiments, the actual velocities being of the same order as those referred to in fig. 2; but if account be taken of the intensity of the light in the Tyndal Cone compared with that of a 100-c.p. lamp placed 20 cm. away, and also to the resistance motion experienced by the particle in air ($\eta = 2 \times 10^{-4}$) compared with that in water ($\eta = 1 \times 10^{-2}$), it will be seen that the forces required to produce the velocities in the experiments are considerably greater than those he records.

It has been noticed by C. G. T. Morison (Proc. Roy. Soc. cviii. p. 280) that soils in suspension showed stratifications on exposure to light, in this case the light being in line with the camera and not at right angles to it as here. He found that the width of the stratifications depended on the colour of the light used; but, so far as I know, he has not published anything further on the question yet. The stratifications have their parallel, in the present work, in the sharp definition of the cloud-surface after exposure; but while in his case the stratifications are definitely created by exposure to light, in the present instance it is only a change of shape of an already existing cloud which takes place. The explanation of the sharp definition of the cloud-edge is not attempted here, but close observation of such a cloud leads one to the opinion that forces in the nature of surface tension of the cloud come into play at the transition from dense to clear solution.

Complete references to other observations on the action of light on the Liesegang phenomenon, including that by Hatschek (Proc. Roy. Soc. xcix. p. 496), are given by Morison in his paper.

My thanks are due to Professor A. W. Porter, D.Sc., F.R.S., for his help in the present work.

Carey Foster Laboratory,
University College, University of London.
13 July, 1926.

*XCIH. Werner's Co-ordination Theory and the Electrical Structure of the Atom. The Relationship between Valency and Co-ordination. By S. H. C. BRIGGS, D.Sc.**

ALTHOUGH the electron theory of valency as developed by Thomson, Kossel, Lewis and Langmuir, Bohr, and others has given an almost complete solution of the valency problem so far as the simpler chemical compounds are concerned, it has not thrown much light upon the structure of the complex substances which were regarded by Werner as co-ordination compounds. The co-ordination compounds also include bodies of varying degrees of polarity, from the strongly polar *crystallized* sodium chloride on the one hand (Pfeiffer, *Zeitsch. anorg. Chem.* xcii. p. 376, 1915; xevii. p. 161, 1916) to the typically non-polar carbon tetrachloride (Werner) on the other. Werner's co-ordination theory is

* Communicated by the Author.

the only *comprehensive* theory hitherto suggested which satisfactorily explains the structure of these various compounds. It is therefore highly desirable that Werner's theory of co-ordination and the electron theory of valency should be correlated. The object of the present paper is to determine the exact relationship between valency and co-ordination, and to show how Werner's theory of co-ordination can be derived from the electrical theory of atomic structure.

WERNER'S THEORY.

A detailed account of the co-ordination theory is given in Werner's book, 'Neuere Anschauungen auf dem Gebiete der anorganischen Chemie' (3rd ed., 1913: Vieweg & Sohn Braunschweig) and also in the papers (*Zeitsch. anorg. Chem.* iii. p. 267, 1893; viii. pp. 153, 189, 1895). Werner regarded the affinity of an atom as an attractive force directed from the centre of the atom equally towards all parts of the surface of the atomic sphere. In Werner's own words ('Neuere Anschauungen,' p. 83): "Der bei gegenseitiger Bindung zweier Atome abgesättigte Affinitätsbetrag verteilt sich auf einen bestimmten kreisförmigen Abschnitt der Kugeloberfläche der Atome (Bindfläche) und wird mit der Natur dieser Atome in weiten Grenzen wechseln." Werner made a distinction between principal valency (Hauptvalenz) and subsidiary valency (Nebenvaleanz). In platinic chloride PtCl_4 the chlorine atoms are attached by principal valencies. The platinum atom, however, is unsaturated and can combine by subsidiary valencies with two molecules of ammonia, to give the compound $\text{Pt}_{\text{Cl}_4}^{2\text{NH}_3}$, in which none of the chlorine atoms is ionizable, the ammonia molecules and the chlorine atoms all being in direct union (direktur Bindung) with the platinum atom. The addition of ammonia molecules in this manner is termed "Anlagerung" (apposition). The compound $\text{Pt}_{\text{Cl}_4}^{2\text{NH}_3}$ can react with a further quantity of ammonia, the chlorine atoms being successively displaced by ammonia molecules until the compound $(\text{Pt}6\text{NH}_3)\text{Cl}_4$ is obtained, in which all the ammonia molecules are in direct union with the platinum atom; but the chlorine atoms are now in an outer zone and are all ionizable, being in indirect union (indirekter Bindung) with the platinum. This process of displacement of chlorine atoms by ammonia molecules

is termed "Einlagerung" (intercalation). In the compound $(\text{Pt}6\text{NH}_3)\text{Cl}_4$ the six molecules of ammonia together possess an amount of affinity equal to that of the platinum atom in PtCl_4 , and the chlorine atoms are thus held in position in the outer zone (*Zeitsch. anorg. Chem.* iii. p. 324, 1893).

In the series of compounds $(\text{Pt}6\text{NH}_3)\text{Cl}_4$, $(\text{Pt}4\text{NH}_3\text{Cl}_2)\text{Cl}_2$, $(\text{Pt}3\text{NH}_3\text{Cl}_3)\text{Cl}$, $(\text{Pt}2\text{NH}_3\text{Cl}_4)$, $(\text{PtCl}_5\text{NH}_3)\text{K}$, and $(\text{PtCl}_6)\text{K}_2$, all of which are known, there are six atoms or groups, in every case in direct union with the platinum atom. Platinum is therefore said to have a maximum co-ordination number six. The maximum co-ordination number is defined by Werner as follows ('*Neuere Anschauungen*,' p. 58):—"Die maximale Ko-ordinationszahl muss als Raumzahl aufgefasst werden, d. h. als Zahlenbegriff, der angiebt, wieviele Atome bestimmter Art sich in der ersten Sphäre eines anderen Elementaratoms räumlich anordnen können."

Werner showed that the maximum co-ordination numbers in the cases of different elements are either four, six, or eight. These numbers represent the apices of the three simplest regular polyhedra, thus emphasizing the essentially geometrical character of the conception of co-ordination, the co-ordinated atoms or groups being arranged symmetrically in space around the central atom.

ELECTRON THEORIES OF CO-ORDINATION COMPOUNDS.

The theory of valency of Lewis and Langmuir does not lead to any very definite conclusions with respect to co-ordination. As Langmuir has shown (*J. Amer. Chem. Soc.* xli. pp. 928-931, 1919), co-ordination compounds may equally well be regarded as electrovalency or covalency compounds.

The most interesting application of the electron theory of valency to co-ordination has been made by Sidgwick (*J. Chem. Soc.* cxxiii. p. 725, 1923). Sidgwick suggests that the element which acts as the central atom in the complex assumes the same external electron configuration as the inert gas which follows that element in the periodic table, each co-ordinated atom or group being united to the central atom by a bond of two electrons (covalency) such as is present in organic compounds. As examples, we may consider di- and trivalent chromium, di- and trivalent iron, and di- and trivalent cobalt, all of which give compounds with co-ordination number 6. Sidgwick's rule applies to the compounds of divalent iron and trivalent cobalt, but fails with trivalent iron, divalent cobalt, and

all the chromium compounds. Since, however, the co-ordination number is 6 in all cases, it is reasonable to conclude that the *dominating* factor in the formation of co-ordination compounds is the tendency to produce spatially symmetrical structures, the actual co-ordination number being determined by geometrical considerations, in accordance with Werner's original views, and further that the formation of the electron configuration of an inert gas is a *subsidiary* factor only. When the two factors coincide, however, the compounds obtained possess a high degree of stability, and it was to such bodies rather than to co-ordination compounds in general that Sidgwick applied his theory.

Prideaux ('Chemistry and Industry,' xliv. p. 25, 1925) defines co-ordination compounds as compounds "whose formulæ . . . contain one or more mixed bonds." This definition appears to be inaccurate, as it excludes bodies such as SF_6 and CCl_4 , which were regarded by Werner as typical, being co-ordinatively saturated ('Neuere Anschauungen,' p. 98).

It should also be observed that if in *all* co-ordination compounds the co-ordinated groups are linked to the central atom by two electrons equally shared, as suggested by Sidgwick and also by Lowry ('Chemistry and Industry,' xlii. pp. 318, 412, &c., 1923) and Brockman ('Chemistry and Industry,' xliii. p. 756, 1924), then co-ordination compounds in general should have a degree of stability comparable to that of organic compounds. This is by no means the case, many true co-ordination compounds being highly unstable. It would therefore appear that any *general* theory of co-ordination based upon the arrangement of electrons around the central atom must of necessity be extremely complicated and difficult. After a critical examination of Sidgwick's theory, J. D. Main Smith concluded ('Chemistry and Industry,' xliv. pp. 944, 1925):—"It appears probable that the maximum co-ordination number is totally unrelated to the size of any group or sub-group in any atom. The experimental evidence points to the conclusion emphasized by Werner that the co-ordination number is governed chiefly by the number of atoms that can be accommodated at the surface of the co-ordinating atom."

In the following pages it is shown that the co-ordination theory as originally established by Werner follows naturally with very slight modifications from the conception of an atom as a combination of electrons with a central positive

nucleus. The point of view adopted is that of the theory of duplex affinity which I have developed in detail in previous papers (J. Chem. Soc. xciii. p. 1564, 1908; xli. p. 253, 1917; cxv. p. 278, 1919; cxix. p. 1876, 1921; Phil. Mag. xlii. p. 448, 1921). A number of general conclusions are drawn with reference to the properties of co-ordination compounds, and in the concluding section the exact relationship between valency and co-ordination is discussed.

THE THEORY OF DUPLEX AFFINITY.

In the combination of potassium and chlorine to form potassium chloride, an electron is transferred from the potassium atom to the chlorine atom. Potassium is generally regarded as an element with positive affinity, and chlorine as an element with negative affinity. In terms of the electron theory we can therefore define positive affinity as a tendency to lose electrons, and negative affinity as a tendency to gain electrons.

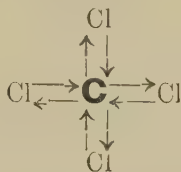
The potassium atom which has lost an electron becoming a potassium ion has now a positive charge. But a positive charge attracts electrons, and therefore, by definition, the potassium *ion* has negative affinity, whereas the potassium *atom* has positive affinity. Similarly, the chloride ion which carries one negative charge has now a tendency to give up an electron to a positive charge, and therefore the chloride ion, by definition, has positive affinity.

We may describe the affinity of the atom as primary affinity and the affinity of the ion as secondary affinity, because the affinity of the ion is a secondary phenomenon which only appears after the affinity of the atom, that is to say the primary affinity, has come into action.

Potassium is therefore an element with primary positive affinity and secondary negative affinity, whereas chlorine is an element with primary negative affinity and secondary positive affinity, so far as the mutual relationship of the two elements is concerned.

The saturation of the affinity may be represented by an arrow pointing from positive to negative. Thus for the combination of potassium and chlorine we write $K \longrightarrow Cl$, the *thick* arrow indicating the passage of an electron from potassium to chlorine. The combination of the two ions K^+ and Cl^- to give a molecule may be written $K^+ \longleftarrow Cl^-$, the arrow again pointing from positive to negative, but a *faint* arrow being used in this instance because no passage of electrons occurs. Combining the two formulæ,

we have $K \longleftrightarrow Cl$ for a molecule of potassium chloride. If the primary and secondary affinities are *equally* saturated, the formula must be written with two thin arrows pointing in opposite directions, since no transfer of electrons takes place in this case, which represents electron-sharing or non-polar union. As an example of a non-polar compound we may write carbon tetrachloride



Attention should now be directed to an important difference between secondary negative affinity and secondary positive affinity. Since atoms are incapable of interpenetration, each atom, so far as its effect on other atoms is concerned, may be regarded as a sphere with the nucleus at the centre. In a positive ion the charge is situated in the nucleus, and therefore, so far as the effect on other atoms is concerned, the attractive force due to this charge (the secondary negative affinity) may be regarded as distributed equally over the surface of the atomic sphere. A negative ion, on the other hand, has the charge on the electrons of the outer shell, and consequently secondary positive affinity is not distributed equally over the atomic surface. It may, indeed, be divided up equally among all the electrons of the outer layer as in a free negative ion such as Cl' , but, on the contrary, it may also be confined to two electrons only, as in bodies such as CCl_4 and SF_6 , in which each halogen atom is united to the central atom by a pair of electrons equally shared.

We see, therefore, that Werner's original conception of chemical affinity as an attractive force directed from the centre of the atom equally towards all points of the surface of the atomic sphere, applies in *all* cases with secondary negative affinity. The conception does not apply to secondary positive affinity in those instances in which the electrons are equally shared, as in CCl_4 . When the secondary positive affinity is divided up equally among all the external electrons, however, the general effect is equivalent to an attractive force emanating from the centre, which is Werner's conception (see Kossel, 'Valenzkräfte und Röntgenspektren,' 2nd ed. p. 15, 1924 : Julius Springer, Berlin).

It is significant that the majority of complexes have a positive atom at the centre. This is no doubt attributable to the fact that secondary negative affinity is *always* distributed equally over the surface of the atomic sphere in contradistinction to secondary positive affinity.

THE FORMATION OF COMPLEX COMPOUNDS.

From the truly non-polar character of carbon tetrachloride we may conclude that the geometrical conditions are such that the secondary affinities of the carbon and chlorine atoms are completely saturated. The case is different with platinum tetrachloride, the platinum atom (and therefore the chlorine atoms as well) being partially unsaturated. The platinum atom may consequently combine with two molecules of ammonia, the link being formed by electrons in the nitrogen octet, giving the compound $\text{Pt}_{\text{Cl}_4}^{2\text{NH}_3}$, an example of the process called "Anlagerung," by Werner.

In the compound PtCl_4 , and therefore also in $\text{Pt}_{\text{Cl}_4}^{2\text{NH}_3}$, the chlorine atoms possess unsaturated secondary positive affinity, and will be attracted by the secondary negative affinity of the hydrogen in such molecules as water and ammonia. The attraction of the water molecules is not sufficiently great to cause the chloride ions to dissociate from the complex to any marked extent in the cold, freshly-prepared solution; but on boiling with a solution of ammonia, chloride ions are removed from the complex and their places taken by ammonia molecules—an example of Werner's process of "Einlagerung."

We may now consider the case of a strong electrolyte (a strongly polar compound) such as sodium chloride. In the isolated molecule NaCl , where the atoms are side by side, only a comparatively small portion of the surface of the atomic sphere of each ion comes under the immediate influence of the other ion. That portion of the atomic surface which is affected corresponds to Werner's "Binde-fläche." The rest of the surface of each atomic sphere may be regarded as unsaturated. When such a molecule is dissolved in water the secondary negative affinity of the unsaturated sodium ion attracts the electrons of the oxygen in the water molecules, whereas the secondary positive affinity of the unsaturated chloride ion attracts the hydrogen nuclei of the water molecules. Water molecules therefore

crowd round each ion (are co-ordinated round each ion), and in the course of thermal agitation the ions separate in the hydrated condition, the process being exactly as assumed by Werner.

In the vapour of sodium chloride, individual molecules are present, as shown by vapour-density determinations. When such a vapour cools down to the liquid and then to the solid state, since the ions are unsaturated in the individual molecules, the molecules will arrange themselves in such a manner that chloride ions surround the sodium ions, and sodium ions surround the chloride ions, giving finally a space-lattice built up of two kinds of interpenetrating complexes having the formulæ (NaCl_6) and (ClNa_6) , as shown by X-ray analysis of the crystals. In other words, the compound crystallizes by polymerization, the new polymerized molecule comprising the whole crystal (see *Phil. Mag.* xlvii. p. 702, 1924).

When sodium chloride and platinic chloride react with each other, two chloride ions from the sodium chloride combine with each molecule of platinic chloride giving the compound Na_2PtCl_6 , a further example of co-ordination. In the complex (PtCl_6) the central platinum atom has four positive charges, and the secondary negative affinity due to these charges is distributed over the surface of a comparatively small sphere. The complex is therefore markedly stable in solution. In the complex (NaCl_6) in the crystal of sodium chloride there is only one positive charge on the central atom, and, since the atomic volume of sodium is much greater than that of platinum, the secondary negative affinity due to this single charge is spread over the surface of a comparatively large sphere. The complex is therefore unstable and breaks up when the crystal is dissolved.

From these examples we see that co-ordination is involved in the solution and crystallization of strong electrolytes as well as in the formation of complex compounds.

In the formation of such a complex as $(\text{Co}6\text{NH}_3)^{+++}$ it should be observed that when the secondary negative affinity of the central atom is saturated by the secondary positive affinity of the nitrogen atoms, a corresponding amount of secondary negative affinity is liberated at the hydrogen nuclei. Hence, whereas the secondary negative affinity was distributed over the sphere of the cobalt atom in the ion Co^{+++} , in the complex ion $(\text{Co}6\text{NH}_3)^{+++}$ (assuming complete saturation of the Co) the same amount of affinity is now divided up among eighteen hydrogen atoms which must be regarded as lying on the surface of a much larger sphere. This is in strict accordance with Werner's original

theory, in which the charge was supposed to be distributed over the surface of the complex ion. We might therefore expect to find that additional molecules of ammonia can be added to the complex $(\text{Co}6\text{NH}_3)^{+++}$, and that these will arrange themselves outside the six already present and be much less firmly attached than the first six. Such compounds have been quite recently prepared by Ephraim (*Zeit. anorg. Chem.* cxlvii. p. 25, 1925), who finds that the substance having the formula $(\text{Co}6\text{NH}_3)\text{Cl}_3, 6\text{NH}_3$ decomposes at -24° .

Lowry ('Chemistry and Industry,' xlii. pp. 316, 412, 462, &c., 1923) has suggested that in a negative complex such as $(\text{PtCl}_6)^{-}$ the two negative charges are situated on the central atom, *i. e.* on the most electropositive atom in the complex. This somewhat remarkable conclusion results from the assumption that each chlorine atom is united to the platinum by a pair of electrons *equally* shared. Electrons need not always be shared equally, however (Fajans, *Naturwissenschaften*, xi. p. 165, 1923; Knorr, *Zeitsch. für anorganische und allgemeine Chem.* cxxix. p. 109, 1923; Briggs, *Phil. Mag.* xlvii. p. 702, 1924); and if the sharing is such that the secondary negative affinity of the platinum atom is fully saturated, each chlorine atom will then be left with some unsaturated secondary positive affinity. Chlorine atoms in this condition will be attracted by the hydrogen nuclei of water molecules in aqueous solution, and will therefore exhibit some slight tendency to dissociate from the complex being replaced by water. I showed some years ago that such very stable complexes as the ferrocyanide and the ferricyanide ions are dissociated in this way, their solutions containing a small amount of the corresponding aquopentacyano-complex (*J. Chem. Soc.* cxvii. p. 1026, 1920). The charge in the negative complexes would therefore appear to be distributed over the surface of the outer zone in accordance with Werner's theory rather than in the central electropositive atom as assumed by Lowry.

From the considerations put forward in this and the preceding sections of the present paper, it is seen that complex compounds are formed as the result of the action of secondary affinity, whereas the simpler binary compounds arise from the action of primary affinity. As the various electron theories of valency deal essentially with primary affinity phenomena, it is not surprising that they are of so little aid in elucidating the structure of complex compounds. It also follows that primary and secondary affinity correspond to Werner's Haupt- and Nebenvalenz (principal and

subsidiary valency) ; but whereas Werner's two types of valency did not differ in sign, as we have already seen, it follows from the electron theory that primary and secondary affinity are opposite in sign. The difference between Werner's Haupt- and Nebenvalenz is never very clear, and disappears entirely in such a compound as $K_2(PtCl_6)$, in which all the chlorine atoms are equal. It should therefore be noted that if we ignore the passage of electrons and regard all compounds as being built up of ions rather than atoms, the difference disappears from the electron point of view exactly as with Werner's theory.

Seeing that the secondary affinity of the central atom in a complex is distributed equally over the surface of the atomic sphere, it follows that for maximum saturation the co-ordinated atoms or groups must be arranged symmetrically in space around the sphere. We therefore have the maximum co-ordination numbers referred to above, to which should be added the number 2 as the co-ordination number of hydrogen, in view of Lowry's work (Lowry and Burgess, J. Chem. Soc. cxxiii. p. 2111, 1923).

THE PROPERTIES OF COMPLEX COMPOUNDS.

The principles put forward in this paper make it possible to deduce some general rules with reference to the properties of complex compounds. Some, though not all of these rules, have been mentioned in the previous papers referred to above, but they are brought together for the first time in a complete form.

(1) Since the limiting case of the strongest possible electrolyte may be represented by the formula $A \longrightarrow B$, and a non-electrolyte by $A \longleftrightarrow B$, it follows that, if we diminish the secondary affinity bond in any compound AB, the tendency to electrolytic dissociation will be increased. The secondary affinity bond may be diminished by building a complex around A or B, because, as we have seen above, in the complex the secondary affinity is distributed over a much larger spherical surface than in the simple binary compound, and the attractive force on the "Bindefläche" will be correspondingly decreased. We therefore have the general rule that

A complex electrolyte is a stronger electrolyte than the simple electrolyte from which it is derived . . . (1)

Examples:—The weak bases $Ni(OH)_2$, $Cu(OH)_2$, $Zn(OH)_2$, &c., by combination with ammonia give complex bases as

strong as the alkalis, and the extremely weak acid HCN gives the very strong complex acids $\text{H}_3(\text{Co}(\text{CN})_6)$, $\text{H}_3(\text{Fe}(\text{CN})_6)$, $\text{H}_4(\text{Fe}(\text{CN})_6)$, &c.

(2) In a series of compounds AB , $\text{AB}_2 \dots \text{AB}_x$ the charge on A increases with increase in valency. Therefore as the valency increases, the secondary negative affinity of A increases also, until we finally reach a stage in which it is sufficiently strong to pull an electron out of an anion B. A limit is thus placed to the value of x and to the valency of A. If, however, we saturate part of the secondary negative affinity of A by building up a complex around A, we can then increase the value of x . We therefore have a general rule to the effect that

In the highest valencies of an element the complex compounds are more stable than the simpler compounds from which they are derived (2)

As examples it may be noted that although CoCl_3 cannot be prepared, $(\text{Co}6\text{NH}_3)\text{Cl}_3$ is a very stable substance, and that the plumbichlorides are a very well-defined class of compounds, although PbCl_4 is highly unstable. The only exceptions to this rule appear to be the compounds of *o*-phenanthroline and α -dipyridyl with ferric salts (Werner, 'Neuere Anschauungen,' p. 66), which easily change into ferrous compounds, possibly owing to the action of Sidgwick's rule, referred to above (p. 1028).

(3) The stability of the higher valencies may also be increased in another manner. In weak acids the secondary affinities are more fully saturated than in strong acids, the limiting case of the strongest possible acid having the formula $\text{H} \longrightarrow \text{X}$, whereas the weakest possible acid would be non-polar, as shown by the formula $\text{H} \longleftrightarrow \text{X}$. Consequently in the salts of weak acids the secondary negative affinity of the metal will be more fully saturated than in the salts of strong acids, from which it follows that

In the highest valencies of a metal the salts with weak acids have a tendency to be more stable than the salts of strong acids (3)

This explains why it is possible to prepare solutions and derivatives of cobaltic acetate but not of cobaltic chloride. A significant exception to the rule is found in ferric cyanide, which loses some cyanogen with the greatest ease. If ferric cyanide has the formula suggested in a former paper (Trans.

Chem. Soc. cxvii. p. 1028, 1920), it is possible that this exception is also due to the working of Sidgwick's rule*.

(4) Owing to the increase of the secondary negative affinity of a metal with increase in valency, it follows that

With increase in valency the maximum co-ordination number tends to increase, and in those cases where the co-ordination number does not increase the complex compounds are the more stable the greater the valency of the central atom (4)

As examples we find that platinum in the platinous salts has co-ordination number four, and in the platinic salts co-ordination number six, and also that in the cobaltic compound $(\text{Co}6\text{NH}_3)\text{Cl}_3$ the ammonia molecules are much more firmly attached than in the corresponding cobaltous compound $(\text{Co}6\text{NH}_3)\text{Cl}_2$.

(5) Consider a series of hydroxides $\text{M}.\text{OH}$, $\text{M}(\text{OH})_2$, &c. Since the secondary negative affinity is spread equally over the surface of the atomic sphere, the attractive force increases at every point of the atomic surface with increase in valency of the central atom. Therefore as we pass from $\text{M}(\text{OH})$ to $\text{M}(\text{OH})_2$, not only do we add a second hydroxyl group, but the first hydroxyl group is more firmly attached in the dihydroxide than in the monohydroxide, because of the increase in the secondary negative affinity of that part of the surface of M which comes under the influence of the first hydroxyl. Consequently, as the valency of M increases, the oxygen atoms become more and more firmly attached. But as the secondary negative affinity of the oxygen is increasingly taken up by the central atom, the intensity of the bond between the oxygen and the hydrogen ion is diminished. Therefore

As the valency of an atom increases, its hydroxides tend to become decreasingly basic or increasingly acidic. (5)

The compounds of manganese and the oxy-acids of nitrogen and of chlorine are well-known examples of this rule (compare Trans. Chem. Soc. cxv. p. 287, 1919).

(6) Again, in any series of compounds AB , $\text{AB}_2 \dots \text{AB}_x$, where A is a positive element and B is a negative element, as we pass along the series the B ions become more and more firmly attached with increase in the valency of A , as shown

* Alternatively, the case may be similar to that of $\text{Cu}(\text{CN})_2$ and $\text{Cu}(\text{NO})_2$, the instability of which has been explained by Fajans (*loc. cit.*).

in the last paragraph. It therefore follows that

The polar properties of the members of a series $AB, AB_2 \dots AB_x$ decrease with increase in valency of the central atom. (6)

Many examples are found in the metallic halides: thus $SnCl_2$, $SbCl_3$, and VCl_3 are solids, whereas $SnCl_4$, VCl_4 , and $SbCl_5$ are liquids at the ordinary temperature.

(7) Since secondary negative affinity is distributed equally over the surface of the atomic sphere, the optimum conditions for complete saturation of the secondary negative affinity of the central atom will be attained when the co-ordinated atoms are sufficiently numerous to influence directly all parts of the atomic surface of the central ion, and when they can be distributed symmetrically in space around the central ion. Consequently

Compounds of the type AB_x will be most likely to exhibit non-polar properties when $x=4, 6$, or 8 , corresponding to arrangement of the B atoms around the A atom at the corners of a regular tetrahedron, a regular octahedron, and a cube respectively. (7)

Examples:— CCl_4 , RuO_4 , OsO_4 , SF_6 , WF_6 , and OsF_8 .
(See Trans. Chem. Soc. cxv. p. 281, 1919.)

(8) *If the salts of a metal combine with ammonia or other co-ordinating substance, the avidity will be greater with the salts of strong acids than with the salts of weak acids. (8)*

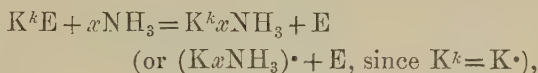
(See Trans. Chem. Soc. xci. p. 263, 1917.)

THE FUNDAMENTAL CHARACTER OF THE CO-ORDINATION PROCESS, AND THE RELATION BETWEEN VALENCY AND CO-ORDINATION.

☞ The atom of an alkali metal consists of a positive ion with one electron revolving around it. At any given instant, therefore, only a part of the surface of the atomic sphere of the positive ion comes under the direct influence of the electron, and the alkali metal, lithium for example, may be regarded as a strongly polar compound analogous to potassium chloride. Writing lithium as a compound of a kernel and an electron, we have Li^kE , Li^k being the lithium kernel and E the electron. As we pass along the series from lithium to neon, we continually increase the charge on the kernel and at the same time we add electrons. In accordance with rule

6 above therefore, as we pass along the series from lithium to neon, the valency electrons should become more and more firmly attached, and the polar properties (that is to say, the electropositive character) of the atom should diminish. This is actually the case, neon having the properties of an ideally non-polar substance.

Further consideration must now be given to the polar character of the metals. From the researches of Kraus (J. Amer. Chem. Soc. xxx. p. 1323, 1908; xxxvi. p. 864, 1914; xliii. p. 749, 1921) it may be concluded that, when an alkali metal is dissolved in liquid ammonia, the ammonia molecules are co-ordinated around the ion of the metal, and dissociation takes place in accordance with the equation; for example,



the free electrons also becoming solvated.

A similar process takes place if the solvent is metallic mercury, because Coehn and Duhem (*Zeitsch. Physik*, xxvii. p. 358), by a study of the electrification produced in gases by bubbling through pure mercury and through mercury containing sodium, obtained evidence of the existence of complex ions $(NaHg_x)^\bullet$.*

In exactly the same way, when potassium is dissolved in water the water molecules are co-ordinated around the potassium ions as explained above (p. 1032), and dissociation into hydrated potassium ions and electrons takes place. The electrons then decompose the water with the formation of

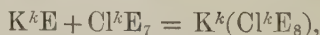
* A compound such as $NaHg_6$ would therefore appear to be an *electride* of a complex sodium mercury base, and the formula should be written $(Na^kHg_6)E$ (compare Phil. Mag. xlii. p. 448, 1921). Other evidence in support of this formula with mercury atoms co-ordinated around the sodium ion is obtained from the recent work of Kraus (J. Amer. Chem. Soc. xlvii. p. 43, 1925), who found that although sodium plumbides and tellurides in which the lead and tellurium are present as anions are readily soluble in liquid ammonia, the compounds of sodium and mercury are insoluble; and this is just what might be expected if the secondary negative affinity of the sodium ion were already saturated by the electrons of the co-ordinated mercury atoms, as in the formula $(Na^kHg_6)E$ (or $(NaHg_6)^\bullet E$). Other substances which may also be regarded as electrides are the compounds of metals with ammonia and with organic bases such as calcium ammonia $(Ca6NH_3)^\bullet E_2$ and sodium pyridine $(Na2C_5H_5N)^\bullet E$, and the free radicles, *e.g.* the monomeric form of tetraethylammonium $(NEt_4)^\bullet E$ of Schlubach and Ballauf (*Ber. der deutsch. chem. Gesellsch.* liv. p. 2811, 1921). Bodies with such a feebly-bound electron are naturally very unstable and reactive, sodium pyridine, for example, being spontaneously inflammable in the air (Emmert, *Ber. der deutsch. chem. Gesellsch.* xlvii. p. 2598, 1914; xlix. p. 1060, 1916).

hydroxyl ions and hydrogen. If a piece of a less electro-positive metal is placed in water, in the course of thermal agitation a few positive ions at the surface, under the attraction of the oxygen of the water molecules, will become sufficiently detached to undergo complete co-ordination, and will be carried away into the solution as hydrated ions. In such a metal, however, the positive ions have a greater charge and a smaller atomic volume than the ions of the alkali metals; the electrons are therefore held more firmly in the metal, and the excess of electrons after removal of the hydrated positive ions remain as a layer of negative electricity on the surface of the metal, being held in position by the attraction of the positive ions near the surface.

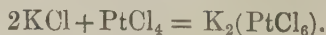
It would appear from these considerations that co-ordination is deeply involved in the phenomena observed when metals are immersed in an ionizing solvent such as water. The actual process that takes place, from this point of view, is a solution of positive ions from the surface of the metal due to an attraction exerted by the molecules of the solvent, rather than to a force driving the ions outward from the metal, an electrolytic solution *pressure*. It may be observed that Langmuir has objected to the conception of a solution pressure on other grounds (*J. Amer. Chem. Soc.* xli. p. 877, 1919; *cf.* Pisarzhevskii, *J. Russ. Phys. Chem. Soc.* liv. p. 778, 1924).

We have now seen the co-ordination process at work in the formation of complex salts, in the solution and crystallization of strong electrolytes, and in the phenomena of electrolytic "solution pressure." The field of action of the co-ordination process extends, however, into the subatomic region as well. According to the modern theories of atomic structure, the electrons or their orbits are arranged around the central positive charge with a high degree of symmetry, and it is significant that the maximum number of electrons in the subgroups of Bohr are 2, 4, 6, or 8—the same as the maximum co-ordination numbers given above, viz. Werner's numbers with the addition of 2 for hydrogen as suggested by Lowry.

Now, if we write potassium and chlorine as compounds of kernels and electrons, the formation of potassium chloride is given by the equation:



with potassium chloride as an *electron co-ordination compound*, the reaction being analogous to the formation of potassium platinichloride:



In an earlier paper (Phil. Mag. xlii. p. 448, 1921) it was shown that all types of chemical compounds may be represented in this manner, their formation being due to the co-ordination of electrons (or electron orbits), so that, in the ultimate analysis, all valency phenomena are based upon co-ordination. It therefore follows that co-ordination, that is to say the symmetrical arrangement in space of electrons (or electron orbits), ions, or molecules around a central kernel or ion, is the fundamental plan according to which all chemical structures are built up.

The relation between valency and co-ordination may also be demonstrated in another way. Suppose, for example, that a number of simple cyanides had been isolated in the pure condition and their combinations with each other had been studied, but that nothing were known with regard to the atoms of which they are composed. Let $a = \text{KCN}$, $w = \text{AgCN}$, $x = \text{CuCN}$, $y = \text{Fe}(\text{CN})_3$, and $z = \text{Fe}(\text{CN})_2$. Then $\text{K}(\text{Ag}(\text{CN})_2) = aw$, $\text{K}(\text{Cu}(\text{CN})_2) = ax$, $\text{K}_2(\text{Cu}(\text{CN})_3) = a_2x$, $\text{K}_3(\text{Cu}(\text{CN})_4) = a_3x$, $\text{K}_3(\text{Fe}(\text{CN})_6) = a_3y$, and $\text{K}_4(\text{Fe}(\text{CN})_6) = a_4z$. We thus obtain what correspond to ordinary valency formulæ for the co-ordination compounds in question; and if a is regarded as monovalent, then w is also monovalent, x is mono-, di-, or trivalent, y is trivalent, and z is tetravalent. Consequently, if the simpler molecules are taken as the units of structure, only valency formulæ are obtained. On the other hand, we have seen above that if the electrons and kernels are regarded as the units, all formulæ become co-ordination formulæ. In chemistry, however, it is customary to take as the units of structure the atoms which represent an intermediate stage between the simpler molecules on the one side and the kernels and electrons on the other. This leads us to the final conclusion that any system of formulating chemical compounds based on the atom as the unit must, of necessity, include both valency formulæ and co-ordination formulæ; and consequently that attempts to devise valency formulæ for the compounds with a co-ordination complex are doomed to failure, a system of valency based upon the atom to include *all* compounds being, in the nature of the case, an impossibility.

April 10th, 1926.

XCIV. *The Flash Arc Spectrum of Potassium.* By F. H. NEWMAN, D.Sc., A.R.C.S., Professor of Physics, University College of the South-West of England, Exeter*.

[Plate XX.]

1. *Introduction.*

THE author has described previously† the excitation of enhanced lines in an interrupted arc passed between sodium-potassium alloy electrodes, the arc lines being extremely faint. The appearance of enhanced lines in the arc is of common occurrence, particularly at that part of the arc in the vicinity of the electrodes, but, as a rule, they are faint. Their great relative intensity in the interrupted arc was attributed to the relatively high potential fall which operated when the arc was started. The electric force in the vicinity of the electrodes, particularly the cathode, is great, and the electrons in these parts may acquire impacting energy between successive atomic collisions sufficient to doubly ionize the metallic atoms, thus giving rise to the enhanced lines. This phenomenon occurs only at low pressures when comparatively few electronic-atomic collisions take place over the short accelerating field constituting the cathode potential fall. The latter must be greater than the minimum voltage through which an electron must fall in order to ionize the surrounding vapour atoms, but it is not always the ionizing potential. If the vapour is non-atomic it is probably identical with the first resonance potential, or the difference between the first resonance potential and the ionizing potential. Although no accurate measurements of the thickness of the region of the cathode fall in arcs have been made, theoretical considerations indicate that it should be about equal to the mean free path of the electrons from the cathode, since they are likely to ionize at first impact, as the electric intensity diminishes with distance from the cathode.

In the case of potassium there are two ways in which the atom may be doubly ionized. The outermost electron may be removed first by impacting energy equal to 4.32 volts, followed by a second collision ejecting an electron from the M ring. On the other hand, the electron from the M ring may be ejected first by the requisite energy—23 volts‡.

* Communicated by the Author.

† Phil. Mag. i. p. 721 (1926).

‡ Mohler & Foot, Bur. of Standards Sci. Paper No. 425 (1921).

The work necessary to remove the second electron from its orbit in the singly ionized atom is 11.5 volts, so that the complete spark spectrum of potassium requires for its excitation the removal of one M electron corresponding to energy 23 volts followed by impacting energy of 11.5 volts through which the outer electron is removed. The complete spark spectrum will therefore make its appearance when the energy is equivalent to 34.5 volts, although the enhanced lines should begin to appear if the impacting energy has a value greater than 23 volts, when the second electron is displaced to an outer orbit but not necessarily ejected from the atom.

In a similar manner it may be proved that the enhanced lines for most elements should appear when the impacting energy is below 50 volts, so that these lines may be expected to occur under favourable conditions in the ordinary arc discharge. Although they do sometimes appear in this manner they are, as a rule, faint, because the actual potential difference across the arc, when the latter is passing, is small, and unless the pressure is very low the mean free path of the electrons is small, so that the accelerating voltage per mean free path of the impacting electron is also likely to be very small. It is evident, however, that in the case of a flash arc at low pressures, *i. e.* an arc which is intermittent, the actual potential difference between the electrodes at each flash or, at any rate, for a period of the duration of the flash, will be the full applied voltage, and if the vapour pressure is maintained at a very low value, conditions are favourable for an appreciable fraction of the electrons to attain energy equivalent to that necessary for the production of the enhanced lines of the vapour. This theory has been tested in the following manner.

2. *Experiments.*

A vacuum arc discharge-tube contained two potassium electrodes, the potassium being packed into glass tubes through which passed iron rods by means of which the voltage was applied. These potassium electrodes were distant apart 5 mm., and a third iron electrode was inserted in the tube so that a momentary electric discharge from a coil could be passed through the tube to start the arc. No external heating was applied. By means of a rotating commutator the arc, when once started, could be quenched and struck alternately, and if the time interval between make and break was small—less than a second—the arc would persist in this intermittent manner. It was assumed that the full applied potential difference, 120 volts, was operative

for at least an appreciable period of the time interval that the arc was in existence. The tube was connected to a pump which, running continuously, maintained the pressure below 10^{-3} mm. of mercury. One end of the tube was closed by means of a quartz window and light from the potassium cathode was focussed directly on to the slit of a quartz spectrograph, the resulting spectrum being photographed on panchromatic plates with an iron comparison spectrum. The spectra obtained in this manner consisted almost entirely of enhanced potassium lines, the arc lines being very faint in comparison, as shown in Plate XX. The chief lines were measured and are given in Table I. No lines appeared below $\lambda=2986$ Å.U. Most of the lines measured occur in the spark discharge obtained by passing a powerful electrodeless discharge through low density vapour.

TABLE I.

The "flash" arc spectrum of Potassium.

Wave-length, λ Å.U.	Intensity.	Wave-length, λ Å.U.	Intensity.
6307	3	4223	6
6247	2	4210	2
6120	4	4202	1
5479	0	4186	8
5464	0	4149	4
5056	2	4135	4
5005	4	4115	5
4829	6	4094	6
4660	2	4058	3
4642	2	4025	3
4608	5	4012	2
4596	0	4009	1
4505	5	4001	4
4467	3	3995	4
4454	4	3967	3
4424	1	3963	2
4388	5	3955	3
4365	4	3943	4
4340	4	3924	3
4309	6	3920	3
4305	4	3898	5
4288	1	3878	1
4263	6	3874	1
4226	6	3862	5

TABLE (continued).

Wave-length, λ Å.U.	Intensity.	Wave-length, λ Å.U.	Intensity.
3818	8	3361.4	3
3801	6	3358.2	2
3783	4	3345.6	5
3767	3	3324.4	1
3745	0	3312.8	3
3739	1	3292.1	3
3722	2	3279.2	1
3716	0	3262.1	1
3682	4	3260.3	0
3676	3	3257.3	1
3669	2	3244.3	1
3636	1	3223.5	1
3627	0	3220.6	2
3618	5	3209.4	1
3609	4	3202.0	2
3555.4	0	3190.0	3
3548.3	0	3170.0	2
3531.0	8	3159.2	1
3517.5	0	3148.0	1
3479.4	0	3129.6	3
3475.2	0	3105.1	4
3440.4	3	3077.0	1
3434.7	2	3062.1	5
3422.3	1	3057.6	0
3404.6	6	3053.1	1
3392.4	1	3035.0	1
3385.3	5	3031.9	1
3381.0	5	3024.6	1
3374.0	5	2993.4	2
3363.2	7	2986.0	1

The configuration of the singly-ionized potassium atom resembles that of the normal argon atom, and it is to be expected therefore that the enhanced spectrum of potassium should resemble in type that of the ordinary arc spectrum of argon. McLennan* has shown that such is the case. Argon emits two types of arc spectra, the red spectrum at moderate excitation and the blue one when intense stimulation is used. McLennan found that the enhanced lines of potassium fell approximately into two divisions with a certain amount of

* Proc. Roy. Soc. A, 100, p. 182 (1922).

overlapping. In the first division, which corresponds with the argon red spectrum, the centre was approximately at $\lambda = 3800$ Å.U., and in the other, corresponding to the blue argon spectrum, the centre was at $\lambda = 2100$ Å.U. As stated above, in the present work no lines below $\lambda = 2986$ Å.U. were observed, so that the spectrum obtained is analogous to the argon red spectrum. This is to be expected when one considers the low excitation voltage used in the experiments, and this result still further emphasizes the similarity, suggested by Sommerfeld, between the normal argon atom and the singly-ionized potassium. Unfortunately the complexity of the argon arc and the potassium spark spectra has prevented this parallelism from being established numerically in a satisfactory manner.

The author wishes to express his thanks to the Royal Society for a Government Grant which enabled this research to be carried out.

XCV. *Researches on the Electric Discharge in Gases and the accompanying Radiation.* By A. DAUVILLIER, Dr. ès Sciences*.

(I.) *Pressure Effects.*

IN a former paper† an hypothesis was put forward to explain the sharp cathodic edge of the negative glow. According to this theory, differences of pressure should exist in the discharge. We have investigated this effect by passing a narrow beam of soft X-rays transversely through the discharge, differences of opacity of the gas being an indication of pressure variations.

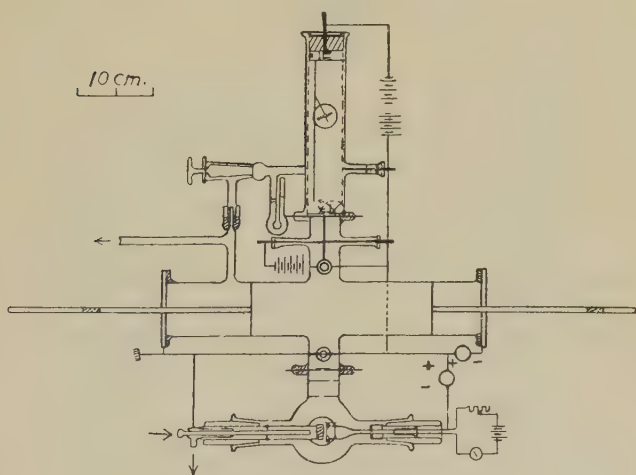
The apparatus, in "pyrex" glass, comprised three parts (fig. 1): the X-ray tube (hot cathode), the discharge tube, and the low-pressure ionizing chamber, for measuring the radiation intensities, separated by very thin celluloid films, which were vacuum tight and of the order of a wave-length of light in thickness. Both the X-ray and discharge tubes were run on a voltage of about 400. The discharge-tube electrodes were movable (magnetic device) so that it was possible to explore any portion of the discharge by means of the X-ray beam.

* Communicated by the Author.

† *Comptes Rendus*, 181. p. 601 (1925).

The gases used were He, Ne, and A, at pressures varying from about 0.1 to 3 mm. Since the intensity of the radiation of the discharge was of the same order as that of the X-rays, this intensity was measured first, that of the combined X-rays and discharge secondly, and that of the X-rays alone thirdly. A comparison of the difference of intensities (2) and (1) with the intensity (3) for the X-rays alone gave an indication of the pressure effect. This effect proved to be feeble, being masked by the presence of a large number of neutral atoms. It was clearly greater (three times)

Fig. 1.



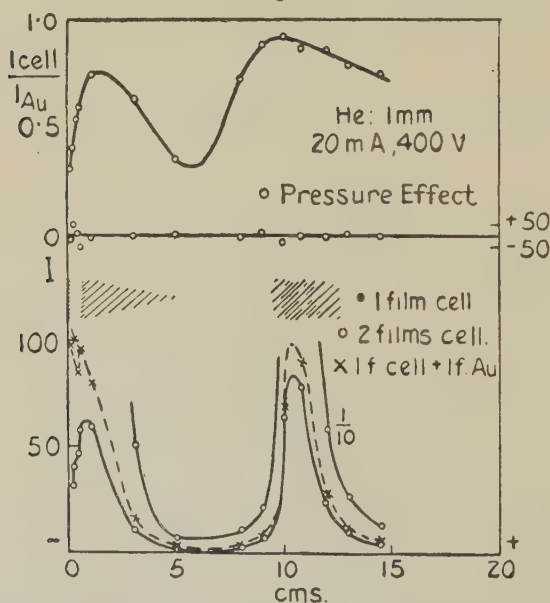
than the possible experimental error only in one point, namely, the sharp cathodic edge of the negative glow, proving the existence of a very considerable density of positive ions. It was always found at this point, located in a thin layer of gas of $\frac{1}{2}$ mm. or less in thickness. A much feebler effect of the same kind was also found at the cathodic edge of the positive column. In no part of the discharge were depressions observed, and these are probably located over large areas, like the Faraday Dark Space. The expected depression in the Crookes Dark Space would appear to have been masked by the double gas current which flows into it. The general trend of the experiments appeared to be in favour of the above.

(II.) Radiations from the discharge.

These radiations, discovered by Wiedemann, were studied by Sir J. J. Thomson *, who arrived at the conclusion that they were of two types: the very absorbable radiation of Schumann, and penetrating X-rays corresponding to the quantum of the voltage applied to the discharge tube.

We have studied the radiation for the different parts of the discharge, characterizing their quality by the filtration exercised by screens—a film of celluloid and a gold-leaf (beaten gold)—placed (magnetic device) in the path of

Fig. 2.

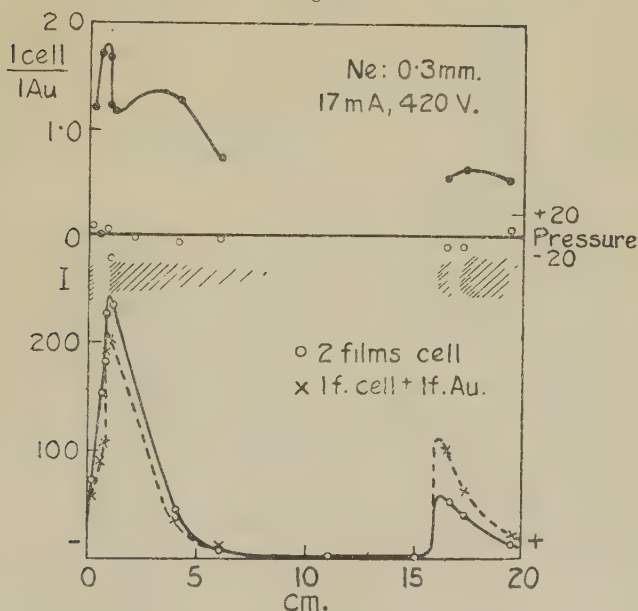


the beam of radiation. Standardization of the radiations was carried out by the X-ray tube running at different voltages. The radiation was in general located in the visible parts of the discharge (fig. 2), with the exception of the Crookes Dark Space, where it is noteworthy. The positive glow invariably consisted of Schumann radiations, the intensity being proportional to the current and independent of the voltage. The quality of the radiation emitted by the negative glow was found to depend, at constant voltage, upon the pressure (fig. 3). When this was of the order of a mm., radiations of a Schumann-Lyman type alone were

* Phil. Mag., July 1924 and May 1925.

observed, but at pressures of about $\frac{1}{10}$ mm. there appeared intense characteristic X-rays of short wave-length, such as the L rays of argon, characterized by their quality and critical potential of excitation (fig. 4). The Crookes Dark Space radiation was remarkable—very soft just in front of the cathode and increasing in penetration towards the edge of the negative glow where it increased brusquely and discontinuously. It thus appears to be due solely to the

Fig. 3.



electrons from the cathode. The negative glow would thus appear as a gaseous anticathode of an X-ray tube with similar laws of emission.

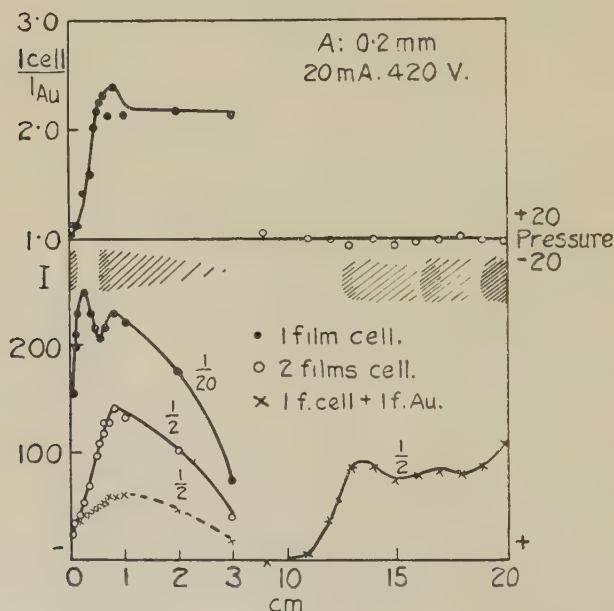
We have not found any appreciable amount of independent Röntgen radiation in the negative glow, as was found in the experiments of Sir J. J. Thomson. The comparison effected by means of the X-ray tube has shown that if this type of radiation exists it is considerably less than that emitted by a solid body*.

* On the contrary, the Schumann-Lyman radiation, which is emitted with very great efficiency by free atoms, is very feeble in the radiation of the solid target. This radiation is responsible—by its photoelectric effect on the cathode—for the *general* cathodic stream (which causes the negative glow) and for the appearance of arc in the thermo-ionic discharge at low potential through gases at very low pressure.

(III.) *The Nature of Soft X-Rays.*

The standardization of the radiations of the discharge naturally led to a study of the nature of the soft Röntgen rays emitted by the X-ray tube. Different authors * had already shown that these formed both qualitatively and quantitatively a continuous spectrum, independent of the nature of the anticathode and devoid of characteristic rays. This result is in opposition to the laws governing X-ray emission in the field of spectrography. We have, on the contrary, observed

Fig. 4.

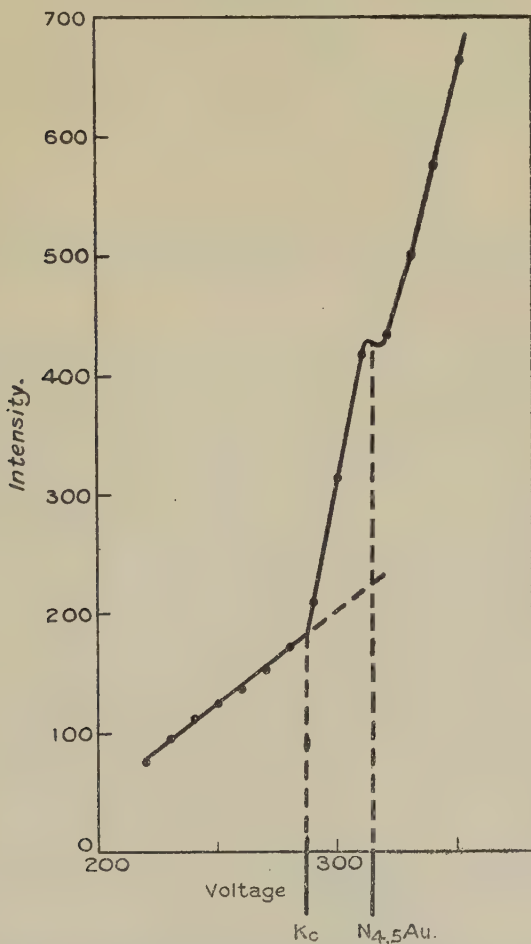


that these rays contained intense characteristic radiations and that they depended largely upon the nature of the anticathode, exhibiting clear discontinuities. Experiments were made with anticathodes of carbon and tungsten. The former showed (fig. 5) emission of K-radiation at 295 volts. For example, at 340 volts the K radiation of carbon was at least three times the intensity of the general radiation. These results were verified by the absorption experiments.

* Cf. Holweck, *Thèses* (Paris, 1920).

We observed, with a tungsten target, many discontinuities which disappeared (fig. 5, lower curve) when the gas pressure in the tube attained a bar and that the output often dropped to a quarter of the normal value for much lower pressures.

Fig. 5.



Ionization-volts graph showing K emission spectrum of carbon
N₄, absorption edge of gold.

This appears to be due to the adsorption on the anode of gas layers which change the intensity of secondary cathode rays impinging on the celluloid window.

The nature of soft X-Rays was later definitely proved by obtaining their spectra: the $K\alpha$ lines of oxygen (24 \AA), carbon ($43\cdot5$), and boron (70) *.

The author wishes to express his indebtedness to Dr. J. Taylor, Rockefeller International Fellow, for his constant and helpful assistance during all the course of the work.

Laboratoire de Recherches Physiques,
sur les Rayons X, Paris.

XCVI. *A Simple Exposition of Electromagnetic Relations.*
By H. F. BIGGS, M.A., M.Sc., Demonstrator in Physics,
Oxford University †.

THE following derivation of the circuital theorems on which Maxwell's equations depend has been developed from the teacher's point of view, but it presents perhaps some points of physical interest.

Now that the objective existence of point-charges has been a familiar idea for a quarter of a century, simplifications may well be made in the exposition of electromagnetic theory by basing it on the fundamental law of the force on a charge moving in a magnetic field. This law is the simplest electromagnetic relation, involves no limits or approximations, is universally true‡, and is directly verified by experiment with considerable accuracy. I doubt if any one stage of the reasoning is new, though many of the arguments are in the converse of the usual order, but I have not been able to find that the scheme has been presented as a whole before.

Fundamental Relation.

The force on a charge e e.s.u. moving with a velocity \mathbf{v} cm./sec. in a field \mathbf{H} gauss is

$$\mathbf{F} = \frac{1}{c} e \mathbf{v} \times \mathbf{H} \text{ dynes.} \quad . \quad . \quad . \quad . \quad (1)$$

* *Comptes Rendus*, 182. p. 927 (Avril 1926); *Bulletin, Sté. fr. Sc. Phys.* (7 Mai, 1926).

† Communicated by the Author.

‡ Apart from quantum mechanics.

Mutual Action between Charge and Pole in Relative Motion.

If \mathbf{H} in (1) be due to a pole m at a distance r from e , we put $H = m/r^2$ and get for the magnitude of the force on e or on m the symmetrical expression

$$F = \frac{vem \sin \theta}{c r^2}, \quad \dots \quad (2)$$

where θ is the angle between \mathbf{r} and \mathbf{v} ; the direction of the forces is perpendicular to \mathbf{r} and \mathbf{v} .

This may, of course, be written in vector notation

$$\mathbf{F} = \pm \frac{1}{c} em \mathbf{v} \times \nabla \frac{1}{r} \quad \dots \quad (2')$$

Now putting $e/r^2 = \mathbf{E}$, the electric intensity at m , we find for the force on m

$$\mathbf{F} = \frac{1}{c} m \mathbf{v} \times \mathbf{E}, \quad \dots \quad (3)$$

\mathbf{v} being still the velocity of e relative to m .

Supposing that e as it moves carries its own field with it, and also that it is only relative motion that matters, we may divide (1) by e and (3) by m , obtaining for the electric intensity due to a moving magnetic field

$$\mathbf{E} = - \frac{1}{c} \mathbf{v} \times \mathbf{H}, \quad \dots \quad (4)$$

and for the magnetic intensity due to a moving electric field

$$\mathbf{H} = \frac{1}{c} \mathbf{v} \times \mathbf{E}, \quad \dots \quad (5)$$

where \mathbf{v} is now in each case the velocity of the field relative to the point considered.

The electromotive force between two near points in a moving magnetic field is then

$$\begin{aligned} \mathbf{E} \cdot d\mathbf{s} &= - \frac{1}{c} (\mathbf{v} \times \mathbf{H}) \cdot d\mathbf{s} \\ &= - \frac{1}{c} (d\mathbf{s} \times \mathbf{v}) \cdot \mathbf{H} \end{aligned}$$

(since the product of three vectors $(\mathbf{a} \times \mathbf{b}) \cdot \mathbf{c}$ is the volume of the parallelepiped \mathbf{abc} , and is therefore a symmetrical function of the three vectors).

But $d\mathbf{s} \times \mathbf{v}$ is the area of the parallelogram whose sides are $d\mathbf{s}$ and the distance moved by the field in one second;

$(\mathbf{ds} \times \mathbf{v}) \cdot \mathbf{H}$ is therefore the magnetic flux crossing \mathbf{ds} per second. Inventing a symbol $\dot{\Phi}_{ds}$ for this quantity, which does *not* mean the rate of increase of any actual quantity Φ , we have

$$\mathbf{E} \cdot \mathbf{ds} = -\dot{\Phi}_{ds}/c.$$

Hence for a complete circuit or path, p , the e.m.f is

$$\oint_p \mathbf{E} \cdot \mathbf{ds} = -\dot{\Phi}_p/c, \quad . \quad . \quad . \quad . \quad (6)$$

where $\dot{\Phi}_p$ means the flux actually crossing the line p per second. This result is obviously perfectly general in spite of the restrictions we have made in the proof.

Precisely similar reasoning, starting from (5), gives for the magnetomotive force round a path p , due to the relative motion of the path of an electric field,

$$\oint_p \mathbf{H} \cdot \mathbf{ds} = \dot{\Psi}_p/c, \quad . \quad . \quad . \quad . \quad (7)$$

where $\dot{\Psi}_p$ is the electric flux crossing p per second.

The equations (4), (5), (6), and (7) must be regarded as universally true (although the relative velocity of path and field is often impossible to determine independently of these relations) whether or not there are charges, currents, etc., in the field. It is only when we come to deal with the *surface* integrals $\Phi = \int \mathbf{H} \cdot \mathbf{dS}$ and $\Psi = \int \mathbf{E} \cdot \mathbf{dS}$ taken over surfaces bounded by p , or rather with their rates of change, that the equations must be modified.

For free space, however, \mathbf{E} and \mathbf{H} being solenoidal, the rate at which flux (magnetic or electric) crosses the boundary p is always equal to the rate of increase of the flux over any surface bounded by p , or of "the flux through p ." We thus have the two circuital relations for free space leading, by Stokes's theorem, to Maxwell's electrodynamic equations for free space

$$\oint \mathbf{E} \cdot \mathbf{ds} = \frac{1}{c} \frac{d\Phi}{dt} = \frac{1}{c} \frac{d}{dt} \left(\int \mathbf{H} \cdot \mathbf{dS} \right) \quad . \quad . \quad . \quad (8)$$

and

$$\oint \mathbf{H} \cdot \mathbf{ds} = -\frac{1}{c} \frac{d\Psi}{dt} = -\frac{1}{c} \frac{d}{dt} \left(\int \mathbf{E} \cdot \mathbf{dS} \right) \quad . \quad . \quad (9)$$

Moreover, since there is no such thing (microscopically speaking) as a free pole, (8) is true universally.

With regard to (9), however, the case is different, since if

there are charges in the field, even stationary ones, we cannot properly speak of *the* electric flux through p at all, the flux over different surfaces bounded by p being different. If there are moving charges, the flux over any one surface changes discontinuously by the amount $-4\pi e$ every time a charge e crosses that surface in the positive direction. While, therefore, (7) remains true, (9) must be modified to take account of moving charges or of currents, if we wish to express the relation by a surface integral. This modification is made by adding to the surface-integral of \mathbf{E} the quantity $4\pi e$ every time a charge e crosses our surface of integration S . This neutralizes the change of flux $-4\pi e$, which has no relation either to the motion of flux across the boundary p or, consequently, to the magnetomotive force, but depends on the position of the surface S , which is quite arbitrary, except as to its boundary.

This can be expressed in symbols if we suppose electric charge to cross S continuously by elements de in time dt , for we then have

$$\oint \mathbf{H} \cdot d\mathbf{s} = \frac{1}{c} \left(\frac{d}{dt} \int \mathbf{E} \cdot d\mathbf{S} + 4\pi \frac{de}{dt} \right),$$

or for a continuous current-distribution

$$\oint \mathbf{H} \cdot d\mathbf{s} = \frac{1}{c} \int (\dot{\mathbf{E}} + 4\pi \mathbf{j}) \cdot d\mathbf{S},$$

where \mathbf{j} is the current density, which includes, of course, the true dielectric displacement current but no "æther displacement current."

If there is no macroscopic change of flux, but only "continuous currents," we have $\dot{\mathbf{E}}=0$, and

$$\oint \mathbf{H} \cdot d\mathbf{s} = 4\pi i/c,$$

where i is the current through p .

So much for the two circuital relations leading to the electrodynamic equations. As to the other two equations of the field, the electrostatic equation, $\text{div. } \mathbf{E}=4\pi\rho$, and the magnetostatic, $\text{div. } \mathbf{H}=0$, the ordinary proof of the former fits into the present scheme, but the latter is more consistently proved thus:—

The magnetic intensity due to a moving charge may be written, by (2),

$$\mathbf{H} = -\frac{1}{c} e \mathbf{v} \times \nabla \frac{1}{r}.$$

Operating by ∇ . gives

$$\text{div } \mathbf{H} = 0.$$

It should be noted that there are assumptions in this argument which imply immediate action at a distance, and are therefore true only for quasi-stationary fields. These assumptions are: (1) the inverse square law for poles and charges, and (2) Newton's third law. It is remarkable, however, that the relations deduced from these assumptions turn out to be universally true when they are relations between quantities existing together in space and time.

In this scheme the ordinary relations between *currents* and magnetic fields are, of course, to be deduced by summing the forces on the moving electrons in an element of wire.

The Electrical Laboratory,
Oxford,
14th May, 1926.

XCVII. *Observations concerning the Artificial Disintegration of Elements.* By J. CHADWICK, Ph.D., Fellow of Gonville and Caius College, Cambridge*.

§ 1. **T**HE first observation of the artificial disintegration of an element was made by Sir E. Rutherford † in 1919, when he found that the passage of swift α -particles through nitrogen was accompanied by the appearance of particles of long range, which he supposed were hydrogen nuclei, or protons, ejected from the nitrogen nucleus by a close collision with an α -particle.

Later, Sir E. Rutherford and the writer ‡ re-examined this effect in nitrogen, and, with the improved methods of counting scintillations then available, it was found that the protons arising from the disintegration of nitrogen by collision with α -particles from radium C had a maximum range in air of 40 cm. Since the maximum range of the swift protons obtained when these α -particles are passed through hydrogen is about 30 cm., this observation showed definitely that no unforeseen contamination with hydrogen could be responsible for the results, and opened the way to the examination of other elements. The element under test was bombarded by the α -particles from a source of

* Communicated by the Author.

† Rutherford, Phil. Mag. xxxvii. p. 538 (1919).

‡ Rutherford and Chadwick, Phil. Mag. xlii. p. 809 (1921).

radium active deposit, and a search was made for H-particles of more than 32 cm. range, that is, beyond the range of any particles due to hydrogen, whether free or in combination, in the material under examination. In this way we found unmistakable evidence of the disintegration of six elements: boron, nitrogen, fluorine, sodium, aluminium, and phosphorus. Many other elements were examined, but no certain evidence of disintegration resulting in the expulsion of protons of long range was found. Attempts were made to prepare materials free from hydrogen and to pursue the examination at absorptions less than 30 cm. of air. The results obtained in these experiments were, however, too indefinite to allow any conclusions to be drawn. It was found that some protons are always present under these conditions, whatever the material under examination, some are emitted from the source itself, and some are due to hydrogen contamination of substances in the path of the α -particles. The examination at small absorptions is further complicated by the presence of long-range α -particles from the source of radium C, which are emitted in such numbers as probably to mask completely the small effect to be expected from disintegration of the bombarded material.

These experiments had, however, shown that the protons liberated in disintegration were emitted in all directions. We* therefore proceeded to search for particles ejected from the bombarded material in a direction at right angles to the direction of the incident α -particles. This method has the advantage that hydrogen in the material no longer affects the results, and also that the number of long-range α -particles scattered at 90° is so small as to be negligible. The examination can thus be pursued with safety down to an absorption corresponding to 7 cm. of air, and with special precautions to still smaller absorptions in the case of the lighter elements. In this way we found evidence of the disintegration of all elements from boron to potassium inclusive, with the two exceptions of carbon and oxygen. We could detect no effect which could be ascribed with certainty to the disintegration of carbon or oxygen. The elements immediately beyond potassium gave somewhat indefinite results. In most cases we observed the liberation of a small number of H-particles, but these appeared to be due to the presence of nitrogen in the materials examined. For example, a piece of Swedish iron gave, on the first

* Rutherford and Chadwick, *Nature*, cxiii, p. 457 (1924); *Proc. Phys. Soc. (London)*, xxxvi, p. 417 (1924).

examination, a small but quite definite number of H-particles. After the iron had been heated in a vacuum for some hours, this effect was reduced to a small fraction of its first value. The effect was therefore attributed to the presence of some active element, probably nitrogen. Similar results were obtained with the other elements in this region between potassium and iron. Experiments with heavier atoms showed that any disintegration effect, if present at all, was very small indeed.

The experiments of Sir E. Rutherford and the writer have shown, then, that all light elements up to and including potassium can be disintegrated by collision with an α -particle of 7 cm. range, with the exceptions of helium, lithium, beryllium, carbon, and oxygen. With these, and with the heavier atoms, we have been able to detect no certain evidence of disintegration as manifested by the expulsion of hydrogen nuclei.

On the other hand, Kirsch and Pettersson * have recently published accounts of experiments which lead to very different conclusions. These workers have observed, under similar conditions to those holding in our experiments, the disintegration not only of those lighter elements such as carbon and oxygen for which we failed to obtain any evidence of disintegration, but of almost every element they have been able to examine. For example, Kirsch and Pettersson find that when carbon, whether as graphite, diamond, or carbon dioxide, is bombarded by α -particles the emission of protons can always be detected. The number of protons obtained from carbon is for very small absorptions about the same as the number they observe from aluminium, but the ranges are much shorter, the maximum range being about 16 cm. in the direction of the incident α -particle, and about 8 cm. at right angles to this direction. These particles should have been recorded in the experiments of Sir E. Rutherford and myself, and it is a very surprising fact that we have been unable to detect them. Our failure to do so is attributed by Kirsch and Pettersson to the low numerical aperture of the microscopes we use for observing scintillations. This explanation, which I shall consider later, is advanced by these authors as the general reason why our observations give no evidence of disintegration in so many cases where they have obtained positive results.

It must be pointed out here that, even in the few cases where both our observations and those of the Vienna workers

* Kirsch and Pettersson, *Wien. Ber.* 1923 and later years. 'Atomzertrümmerung' (Leipzig, 1916).

agree in showing a disintegration effect, the agreement is more apparent than real. We may take as examples the cases of magnesium and silicon. For both these elements Kirsch and Pettersson find a disintegration effect several times greater than we observe, while the maximum ranges of the particles are actually much smaller than we measure. On the supposition that we cannot observe weak scintillations it is to be expected that we should find smaller maximum ranges than Kirsch and Pettersson.

Many more such discrepancies between the Vienna observations and ours might be quoted, but sufficient has been said to show that differences exist of a very serious character. In this paper I shall discuss various points connected with experiments on the artificial disintegration of elements by collision with α -particles, and I shall endeavour to show that we have good reason for holding to the results obtained in this laboratory.

§ 2. *The Optical Systems used in Counting.*

I have mentioned already that Kirsch and Pettersson have suggested, in order to explain the discrepancies between our experiments and theirs, that our optical system is so weak in light-gathering power that we cannot observe the weak scintillations produced by H-particles of low range. Before discussing the question of the minimum energy of the H-particle which can be detected under our conditions of experiment, a few details of our optical arrangement will be given.

It is evident that the first and essential property of a scintillation microscope must be that its light-gathering power should be sufficiently high to enable the observer to count the scintillations with ease and certainty. The second demand to be satisfied is that the field of view should be so large that the scintillations under observation are received in convenient numbers for counting. Further, the magnification of the system should not be less than about $30\times$, for experience shows that with low magnifications some counters fail to observe a fairly large fraction of the scintillations.

In the work in which we are interested here, we have to record chiefly the scintillations due to H-particles of varying ranges. The scintillations are, on the whole, not so bright as those due to an α -particle of a few centimetres range, and those due to H-particles near the end of their range are very weak indeed. The microscope must therefore have a high

numerical aperture. On the other hand, the disintegration of a nucleus by collision with an α -particle is a very rare event, and the number of H-particles received on the screen is usually small, of the order of 1 per minute per sq. mm. of screen. For many reasons it is unsatisfactory to deal with fewer than 20 scintillations per minute, that is, to work with a field of view of less than 10 sq. mm. area. The scintillation microscope must therefore possess not only a high numerical aperture but also a large field of view, two mutually opposed qualities. We have found that the Watson Holographic objective of 16 mm. focal length and $\cdot 45$ numerical aperture satisfies these two conditions sufficiently well for general purposes. The numerical aperture is high enough to enable H-particles of short range to be counted, and a very large field of view can be obtained when a suitable eyepiece is used. For example, an ordinary eyepiece, such as the Watson Holographic, gives with this objective a field of view of about 8 sq. mm. area, while a specially constructed wide-angle eyepiece gives a field of 50 sq. mm. The magnification of the latter system is about $35\times$. We have used this combination for some years and found it quite satisfactory for general use. The scintillations produced by H-particles of short range are very weak, but they can be counted without undue strain and with consistent results. If a higher numerical aperture is desirable, the Watson Holographic objective of 12 mm. focal length and $\cdot 65$ numerical aperture may be used. The scintillations then appear brighter, but the same field of view cannot be obtained.

At the same time we did not ignore the possibility that the above optical arrangement might not be sufficiently powerful to detect very weak scintillations. While it appeared unlikely that one could fail to observe the scintillations due to H-particles of more than a few centimetres range, there was always the possibility that other products of disintegration might be present which might give scintillations too weak to be observed with this system. In order to test this point a special microscope * was constructed for me about two years ago by Adam Hilger and Co. The eyepiece is very similar to that used in the system described above, but the objective is designed solely for the observation of scintillations. A detailed description of this objective will be published later by Mr. Perry, of Adam Hilger and Co., who is responsible for its calculation and design, but a brief account of its main

* The cost of this microscope was covered by a grant from the Caird Fund, for which I am indebted to the Council of the British Association.

features may be given here. In order to keep the numerical aperture as high as possible the first surface of the objective is also the scintillation screen, that is, the zinc sulphide is deposited on the surface of the objective itself. This front surface is hemispherical and about 106 sq. mm. of the surface can be obtained in good focus. The area of the projection of the object-field on a plane perpendicular to the axis of the microscope is about 80 sq. mm. In the correction for extra-axial foci, coma is eliminated, but residual astigmatism remains, the resulting image of a point being sharply focussed as an astigmatic line. This appeared to be the best type of correction possible for the purpose in view, since it is essential to secure the greatest concentration of light in the image. A scintillation which occurs near the edge of the object-field is thus seen as a narrow line of light, whilst those in the centre appear as usual as bright points. The numerical aperture of this objective is 1.06, and the magnification of the system of objective and eyepiece is $\times 32$.

In this microscope there are thus combined a very high numerical aperture and a large field of view, with good definition and a sufficient magnification. It seems unlikely that any considerable improvement could be made in this system. The numerical aperture might perhaps be increased slightly, but only by the sacrifice of a large part of the field of view.

With this special microscope the scintillations, both those of α -particles and those of H-particles, appear much brighter. The improvement is particularly marked in the case of the weak scintillations produced by H-particles of short range. Comparative tests in which this microscope and the old one were used under the same experimental conditions showed however, that while the counting was much easier with the new microscope about the same number of scintillations was observed with both. We found no evidence that scintillations could be observed with the Hilger microscope which were not visible with our old system. We concluded, therefore, that in general our observations of scintillations were trustworthy and that we were not failing to record the existence of particles owing to any weakness in our optical arrangement.

§ 3. *The Efficiencies of Counters.*

A further question arises, however, as to our personal powers of observing scintillations. We have had a long and varied experience in counting scintillations, and our assistants

have been carefully trained. Comparison of the observations of one counter with those of another has revealed only small variations in efficiency, and we have no evidence that one counter can observe scintillations of a type which are invisible to another. The actual efficiency of an observer can be determined by a method due to Geiger and Werner*, which was used by them, in their measurement of the number of α -particles emitted by radium, to eliminate errors of counting caused by fatigue or lack of concentration. The method consists in the simultaneous observation of the scintillations on the same screen by two counters. The zinc-sulphide screen can be observed through each of two microscopes. The area of the screen covered by zinc sulphide is so small that all the crystals are visible through each microscope. Each observer records the occurrence of a scintillation through an electrical contact key on the tape of a chronograph. Now every scintillation which occurs on the screen should be visible to both observers, and, if both are perfect counters, should be recorded at the same time by each, and all the marks recorded by one observer A should coincide with those of the second, B. It is found, however, that all the marks do not coincide; some scintillations are seen by A which are not recorded by B, and *vice versa*. From the tape record of a large number of observations we can deduce both the actual number of scintillations which occurred and the efficiencies of the counters. If N is the number of scintillations which actually occurred on the screen and λ_1 is the probability that the counter A sees and records a scintillation, *i. e.* his efficiency in counting, then on the average he will make $N_1 = \lambda_1 N$ marks on his tape. Similarly counter B will record $N_2 = \lambda_2 N$ scintillations, where λ_2 is B's efficiency. The number of coincidences on the tape, or the number of scintillations which both A and B see, will be $C = \lambda_1 \lambda_2 N$. The record on the tape gives N_1 , N_2 , and C at once, and thus N , the number of scintillations which actually occurred, and λ_1 , λ_2 , the efficiencies of the two counters, can be calculated.

This method of testing the efficiency of counters has been used in this laboratory during the past two years. The microscopes used in these tests consisted of the Watson Holoscope objective of $\cdot 45$ n.a. and a low-power eyepiece. The field of view had an area of nearly 8 sq. mm. About thirty students have been examined, the majority of whom had had no previous experience of counting. When the scintillations are produced by α -particles of a few centimetres

* Geiger and Werner, *Zeit. f. Phys.* xxi. p. 187 (1924).

range, even an untrained observer will count about 80 per cent. of the scintillations, and his efficiency generally rises in a short time to about 95 per cent. With scintillations due to α -particles of not more than a few millimetres range, the untrained observer may count only 60 to 70 per cent. at first, but in the course of time his efficiency will again rise to more than 90 per cent.

A series of experiments has also been carried out on the counting of scintillations due to H-particles. Three observers were used, A and B having had considerable experience in counting, having counted in many of the disintegration experiments, while C was relatively untrained. The source of H-particles was an α -ray tube containing radium emanation. The outer surface of the tube was coated with a layer of paraffin wax of $25\ \mu$ thickness and a sheet of aluminium foil of about 5 cm. stopping power. The H-particles falling on the screen had a maximum range of about 7 cm. in air. As no magnetic field was used to deflect the β -rays emitted by the emanation tube away from the ZnS screen, the screen was much brighter than one would use under normal conditions. In spite of this, the results of the test showed that A counted about 88 per cent., B about 80, and C, the untrained observer, about 60 per cent. of the scintillations.

The conditions in these experiments were much less favourable to accurate counting than in any of our observations of the disintegration particles. These tests therefore give good grounds for the belief that the counting in the disintegration experiments was trustworthy, and that no large fraction of the scintillations present on the screen had been missed *.

§ 4. *The Detection of H Particles of Short Range.*

As far as our experience goes there is, on the average, little difference in the efficiencies of our counters. Occasionally it has been observed that a counter, owing to ill-health or some other temporary cause, has recorded in one experiment consistently fewer particles than the others; but even in such a case the difference has been small. Taking the whole of our counting observations into consideration, we must conclude that one counter can see what

* One point of interest may be mentioned here in connexion with these experiments. When the scintillations appear on the screen at convenient intervals, it is possible for the two observers to compare their impressions of the intensity of the scintillation. It sometimes happens, particularly when dealing with the weaker scintillations, that a scintillation which appears bright to one observer is weak to the other.

is visible to another. This may mean either that particles even of very short range produce a scintillation which can be seen by most observers, or that the limit of vision is about the same for most observers. This question is connected with that of the intensity of the scintillation which can just be detected under the conditions prevailing in our experiments, or rather of the energy of the α -particle or of the H-particle which gives rise to such a scintillation. We already possess a certain amount of information on this point. For example, in the experiments of Bieler and the writer* on the collisions of α -particles with H atoms, scintillations produced by H-particles of about 2.5 cm. range were counted consistently and without difficulty. Again, Sir E. Rutherford† has observed scintillations due to α -particles the velocity of which was only .15 of that of the α -particle of radium C. This velocity corresponds to an energy of only 2 per cent. of that of the radium C α -particle, or to a range of .24 mm. [A proton of the same energy would have a range of about .7 mm.] In both these cases the optical system consisted of a Watson objective of .45 n.a. and a low-power eyepiece, that is, very similar to that used in many of the disintegration experiments. It seems clear, then, that in these latter experiments we should certainly have been able to detect any H-particles of range greater than 3 cm. in air. To make the matter more conclusive, however, a special series of experiments was carried out to test whether, under as far as possible the same conditions as in the disintegration experiments, H-particles of still shorter range could be observed. The H-particles of definite maximum range were produced by the impact of α -particles on H atoms, in paraffin wax in some cases, and in hydrogen gas in others. If the range of a H-particle projected in the direction of the colliding α -particle is R_0 , then the range of the H-particle projected at an angle θ to this direction will be $R = R_0 \cos^3 \theta$. Now both scintillation and ionization measurements agree in giving a value of about 30 cm. of air for R_0 , when the range of the colliding α -particle is 7 cm. If we take $\theta = 45^\circ$ we get $R = 10.6$ cm. Even if the error in R_0 should be as great as 3 cm., the error in R will be only 1 cm. If we use a beam of α -particles of shorter range than 7 cm., the range of the H-particles produced by it will be correspondingly reduced. In this way it is possible to obtain a beam of H-particles the maximum range of which is known with sufficient accuracy. By placing absorbing

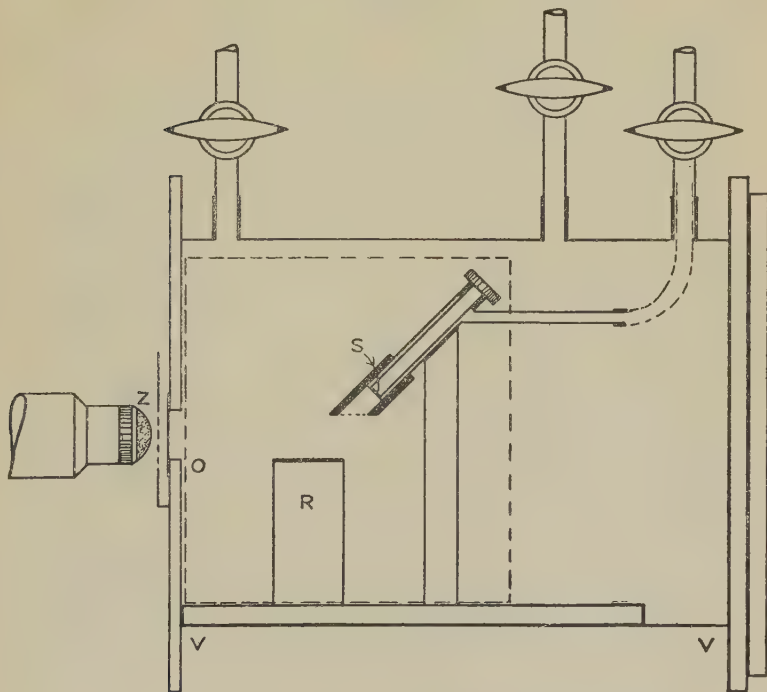
* Chadwick and Bieler, *Phil. Mag.* xlii. p. 923 (1921).

† Rutherford, *Phil. Mag.* xlvii. p. 277 (1924).

screens of mica in the path of this beam we can adjust the maximum range of the H-particles to any desired smaller value. The beams of H-particles defined in this way were received on a zinc-sulphide screen and observed under similar conditions to those prevailing in the disintegration experiments. The experimental arrangement is shown in fig. 1.

The source of α -rays was placed at S in a brass tube with a graphite extension which served to limit the beam of

Fig. 1.



α -rays to a suitably narrow cone. The H-particles were produced in a film of paraffin wax placed on the graphite support R. This support and the source-holder were carried on a slide fitting into the brass box VV. This box could be evacuated. The H-particles produced in the film of paraffin wax were observed on the zinc-sulphide screen Z. The window O in the face of the box, through which the H-particles passed, was covered with a sheet of mica equivalent in stopping power to 2.6 cm. of air. Further

absorbing screens of mica could be inserted between this window and the ZnS screen. A magnetic field was applied to deflect the β -rays emitted by the source away from the ZnS screen.

The source of α -rays was a brass disk of 3 mm. diameter coated with radium active deposit. In order to obtain a beam of H-particles of suitable range, the source was covered with a sheet of mica of 3.35 cm. stopping power. The α -particles incident on the paraffin wax thus had a maximum range of 3.65 cm. The H-particles were observed in a direction at 45° to the direction of the incident α -particles. The maximum range of the H-particles projected in this direction was therefore 5.5 cm. Owing, however, to the finite widths of the cone of α -rays and of the cone of H-particles received on the screen, there were a few particles present with greater ranges, up to 8.3 cm. When the total absorption in the path of the H-particles was 4.3 cm. of air, that is, most of the particles had ranges less than 1.2 cm. while a few still had 4 cm. range, the number of scintillations was comparatively large. When the absorption was increased to 7.0 cm., some scintillations were still observed. That these were due to H-particles from the paraffin wax was shown by replacing the film by a thin sheet of graphite, when no scintillations were observed beyond those due to the natural effect of the screen.

In other experiments the paraffin wax was removed and the box VV was filled with hydrogen at atmospheric pressure. Similar results were obtained, in that scintillations were observed when the maximum range of the H-particles falling on the screen was not more than 6 mm.

Some experiments have been carried out with an apparatus of similar type to that used in the work of Bieler and the writer. In these the H-particles were observed at angles between 60° and 70° to the direction of the incident α -particles. The results again showed that the scintillations produced by H-particles of ranges less than 1 cm. can be counted consistently.

In these experiments both the Watson objective of .45 n.a. and the special Hilger microscope were used. While the greater numerical aperture of the Hilger microscope rendered the counting of these weak scintillations much easier, there was no evidence that with this microscope scintillations were visible which could not be seen with the other. Since in the above experiments H-particles of only a few mms. range were observed consistently by all our counters, it would seem

that the energy necessary to produce a visible scintillation must be extremely small. In other words, the retina of the dark-adapted eye must be able to detect exceedingly small amounts of light. It is possible to form an estimate of the amount of light received by the retina in the observation of a scintillation. For this purpose we may take the observation of Sir E. Rutherford that α -particles of radium C possessing only $\cdot 15$ of their initial velocity still produce a visible scintillation. The energy of such an α -particle is 2.75×10^{-7} erg. Now Marsden* has shown that the visible light of the scintillation contains about 1.5 per cent. of the energy of the α -particle. Hence the energy of the total amount of light emitted in the scintillation observed by Rutherford was about 4×10^{-9} erg. The objective through which the scintillation was viewed had a numerical aperture of $\cdot 45$, and therefore collected about one-twentieth of the total light emitted by the scintillation. The energy finally received on the retina, omitting losses due to reflexion and absorption, was thus about 2×10^{-10} erg.

This result is in general agreement with observations on the sensitivity of the dark-adapted eye made by many workers, in particular by Grijns and Noyons†, and by du Noüy‡. A close comparison with the results of these observers is not possible since the scintillation observations are made under rather different conditions. It may be mentioned, however, that Noyons was able to detect under suitable conditions an amount of white light of about 4×10^{-11} erg. Since the eye is relatively insensitive to light of the longer wave-lengths, Henri and des Bancel§ have concluded that the dark-adapted retina can just detect an amount of green light of energy about 5×10^{-12} erg, roughly one quantum. The visual spectrum of the light emitted in a scintillation in zinc sulphide has its maximum in the green at about $515 \mu\mu$, very close to the region of wave-lengths to which the eye is most sensitive. It seems very probable, then, that we should be able to detect by their scintillations α -particles of even smaller energy than those observed by Rutherford. If we assume that the H-particle is as efficient in producing a scintillation as the α -particle, it appears that we should be able to observe the scintillations due to H-particles of ranges of only a few tenths of a mm. of air.

* Marsden, *Proc. Roy. Soc. A*, lxxxiii. p. 548 (1910).

† Grijns and Noyons, *Müller's Arch. f. Phys.* p. 25 (1905).

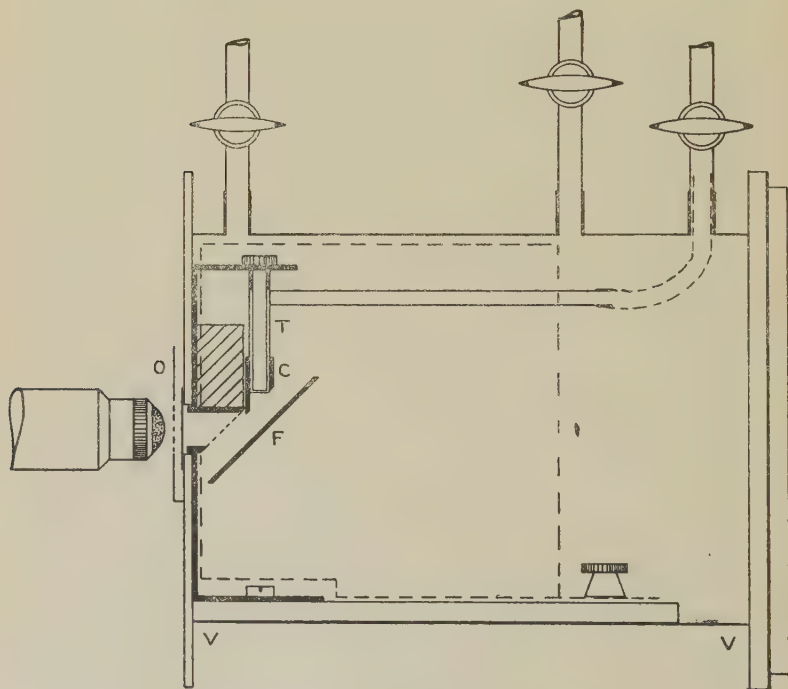
‡ du Noüy, *J. Gen. Phys.* iii. p. 743 (1920).

§ Henri and des Bancel, *J. Phys. Path. Gen.* xiii. p. 841 (1911).

§5. *Experiments on the Disintegration of some Light Elements.*

The experiments described in the last two sections show that our observation of scintillations is reasonably efficient, and that the optical systems used in the disintegration experiments are sufficiently powerful to enable us to detect the presence of H-particles of short ranges. It seems then that the differences between our results and those of Kirsch and Pettersson cannot be explained by their suggestion that

Fig. 2.



our optical arrangement is too weak. Before discussing these differences in further detail I shall now give an account of some recent experiments in which the effects were observed when certain light elements were bombarded by α -particles.

The experimental arrangement will be clear from the diagram of fig. 2, and need not be described in great detail.

The source, a small disk coated with radium active deposit, was enclosed in a brass tube T, which could be evacuated

independently of the box VV. The end of the tube T was covered with a thin sheet of collodion of 2 to 3 mm. air equivalent. A diaphragm C of graphite served to limit the beam of α -particles. The material to be bombarded was placed at F, and was carried on a graphite frame. This was placed in position on slides fixed to two graphite plates (shown by dotted lines). Observations were made at an angle of 90° to the beam of α -particles. The window O in the face of the box was covered with a sheet of mica of 2.6 cm. air equivalent. The zinc sulphide screen, in these experiments the front surface of the Hilger microscope, was brought opposite this window at a distance of about 3 mm. Absorbing screens of mica or aluminium could be introduced between the window O and the ZnS screen. The box was placed between the poles of a magnet in order to reduce the luminosity of the screen caused by scattered β -rays.

As usual in experiments of this kind, precautions were taken against extraneous effects due to scattered α -particles and to contamination. To avoid the presence of scattered α -particles all surfaces exposed to the source were covered with sheets of graphite, except of course the material under examination. Owing to the low atomic weight of carbon, the α -particles scattered at an angle of 90° have a range only .354 of the incident range. The α -particles in these experiments had a range of about 6.8 cm. after passing through the fixed collodion film. The range of the α -particles scattered from the graphite walls at an angle of 90° was therefore 2.4 cm. Such α -particles were completely absorbed in the mica window at O and failed to reach the ZnS screen. Owing to the width of the beam of α -particles it was possible for α -particles to reach the window which had been scattered through only 75° . It was therefore not possible to eliminate completely the extraneous effects below an absorption of about 3.5 cm.

The disturbing effect of contamination was guarded against by enclosing the source in the tube T, and in addition by passing a slow stream of oxygen through the box. The oxygen was led in through a series of fine holes in the face of the box. The pressure of oxygen in the box was between 1 and 2 mm. of mercury. With these precautions contamination was only occasionally observed. Any experiment in which it occurred was rejected.

The results observed in these experiments may be summarized very briefly. When an aluminium foil of 2.6 cm. air equivalent was bombarded, the number of H-particles observed at ranges greater than 8 cm. of air was

nearly 4 per minute per mgm. activity of the source. When the box was filled with dry air to atmospheric pressure and no radiator was used, *i. e.* nitrogen was under bombardment, about 4 to 5 particles per minute per mgm. were observed at an absorption corresponding to 6 cm. of air. These experiments gave a standard with which to compare the results obtained with the other elements to be specially examined, *viz.*, lithium, beryllium, carbon, and oxygen.

A piece of metallic beryllium of a high degree of purity was used. The total absorption in the path of the H-particles was equivalent to 3 cm. of air. An average of ten scintillations per minute was observed, giving nine after deduction of the natural effect of the screen. The activity of the source was 43 mgm. When an extra absorbing screen of 1.3 cm. of air was inserted in the path of the particles, the number of scintillations fell to the natural effect. On replacing the beryllium radiator by a dummy carbon frame, we observed at an absorption of 3 cm. seven scintillations (net) per minute, the source having then decayed to 32 mgm. The effect observed at an absorption of 3 cm. was thus the same when the beryllium radiator was away as when it was present, and it has been pointed out above that a few scattered α -particles might be expected at this absorption. We concluded that the few scintillations observed were due to α -particles scattered at smaller angles than 90° by the carbon surfaces, and that there was no residue to be ascribed to the beryllium. There were no particles present with ranges greater than 4 cm. of air.

Similar results were found with carbon and oxygen. A sheet of Acheson graphite served as a carbon radiator, while for oxygen the box was filled with the gas to atmospheric pressure. In both cases there was no evidence of the emission of H-particles with ranges greater than 4 cm. of air.

The experiments with lithium as radiator were not so definite. At the smallest absorption scintillations were observed to the number of about 1 per min. per mgm. The number decreased rapidly as the absorption was increased, and fell to the natural effect of the screen at a total absorption of 4.3 cm. The scintillations appeared rather bright for H-particles of such short range, and it seems probable that they were due to α -particles scattered by a small sodium impurity in the specimen of lithium. This explanation is supported by the observed range of the particles and by the fact that different samples of lithium gave different numbers of particles under the same conditions

of experiment. We can, however, say definitely that no particles were observed which had ranges greater than 4.3 cm. of air.

These observations confirm the earlier experiments of Sir E. Rutherford and the author in showing no evidence that the nuclei of lithium, beryllium, carbon, and oxygen are disintegrated by collision with an α -particle. The number of H-particles with ranges of more than 4 cm. in air liberated from these elements is certainly less than one-fortieth of the number ejected from aluminium under the same conditions. Pettersson *, on the other hand, found for both beryllium and carbon a relatively large number of H-particles at low absorptions. At an absorption of 4 cm. there were present roughly as many H-particles as we observe from an aluminium radiator, while the maximum ranges of the H-particles observed at 90° to the incident α -particles was about 8 cm. in the case of carbon, about 9 cm. for beryllium. The tests described in the previous sections have shown that our counters are able to observe consistently the scintillations due to H-particles of only a few mms. range. It seems most unlikely that they should all fail to observe those due to H-particles of 4 cm. range, and we are forced to the conclusion that no such particles are present in our experiments.

In the same series of experiments, Pettersson observed the disintegration of silicon. The number of H-particles was roughly the same as for beryllium or carbon, and the maximum range of the particles was only slightly greater, about 10 or 11 cm. of air. Silicon behaves, therefore, according to these results, in a very similar way to carbon and beryllium. One would expect that, if our failure to observe the particles from carbon and beryllium is due to inefficiency of counting, we should fail also to observe the particles from silicon. This, however, is not the case. As we have stated previously, Sir E. Rutherford and the writer have also found that silicon is disintegrated by α -particles. We observed relatively far fewer H-particles than Pettersson, but found that the maximum range was much greater, about 24 cm. of air. Though the agreement between the two sets of observations is more apparent than real, yet the comparison of the results strengthens the conviction that our counting is efficient.

The objection may be raised that the experiments described above offer no evidence as to whether the elements beryllium, carbon, etc., disintegrate with the emission of H-particles of

* Pettersson, *Wien. Ber.* cxxxiii. p. 445 (1924).

very short range. The difficulty in observing such α -particles lies in the presence of the scattered α -particles. While an α -particle of moderate range, say about 2 cm., produces a much brighter scintillation than does a H-particle of the same range, it is difficult in practice to distinguish the scintillations seen on the screen as due to α or to H particles. The beam of scattered α -particles contains α -rays of all ranges up to the maximum scattered range, and those of short range predominate, for although the beam of incident α -particles is homogeneous, the radiator is usually infinitely thick, considered from the point of view of α -ray scattering. The scintillations produced by such a scattered beam will be mainly very weak, with relatively few bright ones. To distinguish separately the scintillations produced by a small number of H-particles superposed on this scattered beam, is, as far as our experience goes, impossible to achieve. We have found it advisable to restrict the investigations for products of disintegration to the region beyond the range of the α -particles scattered from the elements under examination.

The Vienna workers, on the other hand, claim to be able to distinguish the scintillation produced by a H-particle from that due to a scattered α -particle, and, relying on this, they have pursued the search for H-particles to the smallest absorptions, well within the range of the scattered α -particles. This difference in procedure is partly responsible for the difference between their results and ours. To take one example out of many, we may discuss the observations on the disintegration of aluminium.

§ 6. *Comparison of Observations on Aluminium.*

Schmidt *, working in Vienna, found no evidence of a lower limit to the ranges of the H-particles liberated from aluminium, and indeed the majority of the H-particles he observed had ranges less than 4 cm. of air. He also compared the effects when aluminium was bombarded by α -particles of different ranges, and found that H-particles were still liberated when the impinging beam of α -rays had only 1.3 cm. range. The number of H-particles liberated from a thin sheet of aluminium by α -rays of low speed was not smaller than the number found when high speed α -rays were used, but the ranges of the H-particles were shorter.

These results are very different from those obtained in this

* Schmidt, *Wien. Ber.* cxxxiv. (1925). This paper was not available to me. His results are taken from Kirsch and Pettersson, 'Atomzertrümmerung.'

laboratory, where we have observed that the H-particles liberated from aluminium have a minimum range of about 10 to 12 cm. of air, and that α -rays of short range are unable to disintegrate the aluminium nucleus. In our early experiments we observed few, if any, H-particles of range greater than 30 cm. when aluminium was bombarded by α -particles of less than 4.9 cm. range, but did not pursue the examination to smaller absorptions. I have recently re-examined the effect of bombarding aluminium by α -particles of different ranges, using the apparatus shown in fig. 2. The H-particles were therefore observed at right angles to the direction of the beam of incident α -particles, and the observations could be carried down to the range of the scattered α -particles. It was found that as the range of the incident α -particles was reduced, the number of H-particles observed, and also their maximum range, decreased until with α -particles of about 3 cm. range no definite evidence of H-particles could be detected *. The H-particles liberated by α -particles of short range still showed a minimum range of about the same value as observed for those ejected by fast α -particles.

In earlier papers † it has been assumed that the force exerted by the nucleus on a positive charge changes in the nucleus or very close to it, from a repulsive force varying as the inverse square of the distance to one of attraction of more rapid variation. On this view there must be a critical surface around the nucleus at which the force is zero or the potential a maximum. The H-particle emitted from the nucleus in disintegration cannot escape from the nucleus with less final energy than corresponds to the potential at this critical surface. The H-particles must thus have a certain minimum range corresponding to this potential. However the disintegration of the nucleus is brought about, whether by swift α -particles or those of energy just sufficient to produce disintegration, the liberated H-particles cannot have less than this range. Further, no α -particle will cause disintegration unless it has sufficient energy to penetrate within this critical surface. We are thus able from the observations to obtain approximate values for the potential of this surface, both from measurements of the minimum ranges of the liberated H-particles and from the range of the

* It is difficult to fix this minimum range of the effective α -particle with any accuracy. The beams of α -rays of short range are obtained by placing absorbing screens of mica over the source of radium B+C, and since a wide cone of rays must be used in order to obtain a measurable effect the beam is necessarily heterogeneous.

† Rutherford and Chadwick, *loc. cit.*

α -particle which is just able to produce disintegration ; and from this we can make an estimate of the distance of the critical surface from the centre of the nucleus, or of the "size" of the nucleus.

Whatever view one may take of the structure of the nucleus or of the laws of force inside it, one would expect the H-particle emitted in disintegration to possess a minimum range corresponding to the energy gained in its flight down the electrical field of the nucleus, and also corresponding to the energy of the α -particle which is just able to bring about disintegration. Since we know that the law of force is at least approximately that of the inverse square except at very close distances, we can again make some estimate of the "size" of the nucleus.

Interpreting our observations in this way, we find that the aluminium nucleus has a radius of about 8×10^{-13} cm.

The experiments of Schmidt would make the aluminium nucleus much larger, of radius about 20×10^{-13} cm. Indeed, his observation that many of the liberated H-particles have ranges corresponding to less than 1 cm. of air would make the nucleus even larger than this.

It seems to me improbable that the nucleus of aluminium can be so large, for the experiments of Sir E. Rutherford and the writer on the scattering of α -particles have shown that aluminium behaves normally when the distance of collision between the nucleus and the α -particle is about 10 to 12×10^{-13} cm.; the scattering by the silver nucleus, which one would expect to be larger than the aluminium nucleus, is normal for collisions at a distance of 20×10^{-13} cm. These scattering experiments therefore support in a general way our observations on the disintegration of aluminium. It may be objected that Schmidt's observations have been carried further than ours, in that we have made no attempt to search for H-particles of range less than about 3 to 4 cm. of air. On the general views outlined above, one must expect that the H-particle must acquire in falling down the electrical field of the nucleus an energy sufficient to give it a range nearly three times the range of the α -particle which is just effective in producing disintegration. For example, an α -particle of 3 cm. range, if just able to disintegrate the aluminium nucleus, should liberate H-particles with a minimum range of nearly 9 cm. To observe these it is not necessary to pursue the observations within the range of the scattered α -particles.

In my opinion, the difference between our results and those of Schmidt is chiefly due to his procedure in counting

within the range of the scattered α -particles, and in judging from the brightness of the scintillation whether it was due to an α -particle or to a H-particle. As I have stated previously, we have never, in this laboratory, felt confident of our ability to pick out the scintillations of H-particles from those of a heterogeneous beam of α -particles, although we have had considerable experience in counting.

§ 7. *Summary.*

In this paper I have pointed out the conflicting nature of the results in investigations of the disintegration of elements by collisions with α -particles obtained by workers in Vienna and by Sir E. Rutherford and myself. While the former workers find that disintegration with the liberation of H-particles seems to be a common property of all elements, we find that only the lighter elements can be disintegrated and among these there are certain striking exceptions.

Our failure to observe the effects found in Vienna has been attributed by Kirsch and Pettersson to the unsatisfactory optical equipment at our disposal for the counting of scintillations. I have endeavoured to show here that this explanation is without foundation and that we can in fact observe with our microscopes the scintillations produced by any H-particles which are likely to be emitted in the disintegration of a nucleus. Our optical systems have been described, and the results of some tests of the efficiencies of our counters have been given, together with some observations of scintillations due to H-particles of short range.

Experiments have been made to re-examine the elements lithium, beryllium, carbon, and oxygen, but no evidence of disintegration has been detected. These results confirm the previous experiments carried out in this laboratory, but are in sharp disagreement with those of the Vienna workers.

I am unable to suggest any explanation which will account satisfactorily for the differences between these results and those obtained in Vienna. In certain cases it seems possible that their procedure of picking out the scintillations due to α -particles and those due to H-particles by the difference in brightness has led to error. Some of the conflicting results in the investigations of aluminium may perhaps be explained in this way. The main points at issue however, still remain without explanation.

Cavendish Laboratory,
Cambridge.

XCVIII. *Scattering of Positive Rays by Gases.*—II. By
G. P. THOMSON, M.A., *Fellow of Corpus Christi College,
Cambridge, and Professor of Natural Philosophy in the
University of Aberdeen* *.

THE experiments described in this paper are a continuation of those recently published in this magazine † on the scattering of positive rays in hydrogen. The gases investigated are helium and argon, with a few experiments on oxygen. With a few minor modifications, mentioned below, the apparatus is the same as that described in the previous paper, to which reference should be made for details. The following is an outline of the method. A beam of positive rays was obtained by making a fine slit in the cathode of a discharge-tube, and fitting a similar parallel slit some distance behind. This heterogeneous beam then passed between the plates of a condenser, and thus was deflected into an energy spectrum. A small portion of the deflected rays was sorted out by means of a diaphragm with a slit .5 mm. wide, which allowed rays to pass of a certain small range of energy, the average of which could be adjusted at will by changing the potential difference, maintained between the plates of the condenser by a battery of dry cells. The rays thus isolated passed through the scattering chamber (10 cm. long) and struck a photographic plate which could be raised and lowered as required. In the absence of scattering, the developed plate would have shown an approximately uniform blackened strip about 1.8 mm. wide, being the projection by the rays of the .5-mm. slit on the plate. Actually this strip was always bordered by a fainter blackening, due to the rays whose paths had been deflected from a straight line by collisions with the molecules of the gas. The intensities of the scattered rays at various distances from the edge of the main beam were measured photometrically. For the method used to calibrate the plates, and other photographic details, see the previous paper.

Experiments in Argon and Helium.

There was one important difference between these experiments and the previous ones. Previously the rays (protons) were derived from the gas (hydrogen) used for the scattering. In this case it was desired to test the scattering of protons

* Communicated by the Author.

† Phil. Mag. vol. i. p. 961 (1926).

by the inert gases, and it seemed probable at first that different gases would have to be introduced into the discharge-tube to form the rays, and the scattering chamber to scatter them. It was found, however, that the persistence of hydrogen in the positive rays is so great that even after several hours' running, with a stream of argon or helium passing through the apparatus, the hydrogen rays were still far the strongest, as shown by a test exposure which was taken on each plate, with the addition of a magnetic field to form a mass spectrum. No doubt this is partly due to the much greater sensitivity of the photographic plate to the fast hydrogen rays, and probably, if an electrical method of measuring the rays had been used, the result would have been very different. Nevertheless it is remarkable that, in some 60 photographs taken, the helium or argon lines were only visible, and that very faintly, on two or three, in spite of the fact that the spectrum of the discharge showed only helium or argon, as the case might be, and H_{β} . By far the strongest line on the mass spectrum was the H_+ , or proton; the H_{2+} was very faint with helium, and, though rather stronger in argon, was under 15 per cent. of the strength of H_+ except in one or two plates, which were rejected for that reason. In addition, many of the plates showed a faint line at a mass of about 14, though with the very small dispersion available it could not be measured accurately. This is probably due to the layer of air formed on the glass and metal when the apparatus is opened to the atmosphere to change a plate. The traces of air in the spectrum of the discharge were, however, very slight, and it is unlikely that the impurity was sufficient to affect the results to the order of accuracy of the experiment.

The helium used was given me by Sir J. J. Thomson. It was purified before use by fractionation over charcoal in liquid air.

I am indebted for the argon to the Research Department of the General Electric Company. It was 98 per cent. pure, the impurity being nitrogen and oxygen. It was further purified before use by being passed several times over calcium turnings at a bright red heat.

Results.

As in the case of hydrogen, each experiment gives a curve showing the relation between the density of the scattered radiation at any point and the distance of the point from the edge of the main beam. This curve can be used to calculate

the collision relation between a ray and a molecule of the gas. The experiments were made with rays of various velocities and with various pressures in the scattering chamber. It was found that the shape of the curves was the same in both the gases, and was independent of the velocity within the errors of experiment. Thus the intensity at any fixed point of the curve can be taken as a measure of the scattering in investigating the way in which it depends on the speed of the rays.

Variation with Pressure.

In the case of helium it was found that consistent results were obtained by supposing that the scattering was proportional to the pressure, provided that the criterion for "single" scattering (see the previous paper) was satisfied. The results for argon, however, showed great discrepancies, if it was assumed that the scattering was proportional to the pressure as indicated by a McLeod gauge connected with the scattering chamber. The explanation is as follows. For helium, as for hydrogen, a tube filled with charcoal and immersed in liquid air was in close connexion with the scattering chamber through a tap of wide bore. In the argon experiments it was feared that this would lead to too great an absorption of argon, and that the gas left in the scattering chamber would be largely the residual hydrogen from the discharge. Thus the charcoal was turned off, or only used in CO₂ snow. The effect of this was that the vapour from the taps, some of which (such as the one which served as a winch to lower the plate) were unavoidable, was present in the scattering chamber and produced an effect equivalent to about .003 mm. of argon. A similar effect has also been observed by Rückhart *. In consequence of this it was necessary to make observations at a number of pressures, and draw the graph, a straight line, in order to determine the scattering due to the argon itself. A specimen graph is shown in fig. 1. The work thus became very laborious, as, in general, only one photograph can be taken in a day, and some of these have to be rejected owing to changes in the discharge, shown either by changes in the observed pressure or by differences between the blackness of the check exposures at the beginning and end of the series.

Variation of Scattering with Speed of Rays.

However, fig. 2 shows the scattering for helium and

* *Ann. Physik*, lxxiii, p. 73 (1923).

argon plotted against the velocity of the protons. The scattering is measured in arbitrary units and at an arbitrary pressure 4/1000 mm., the same for each gas. The most interesting point about the result is that they show a maximum of scattering at certain speeds. It is surprising

Fig. 1.

Argon 4300 Volts

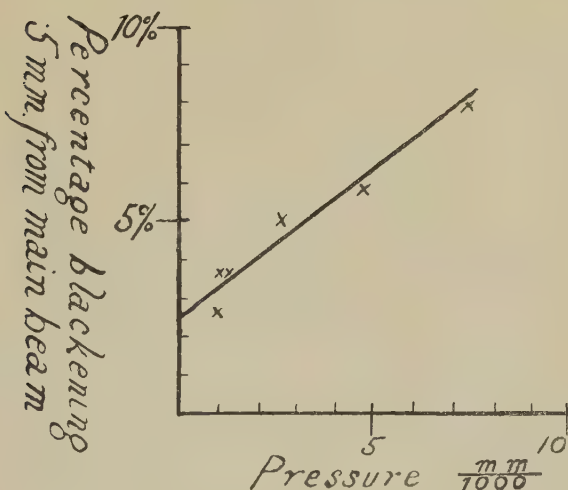
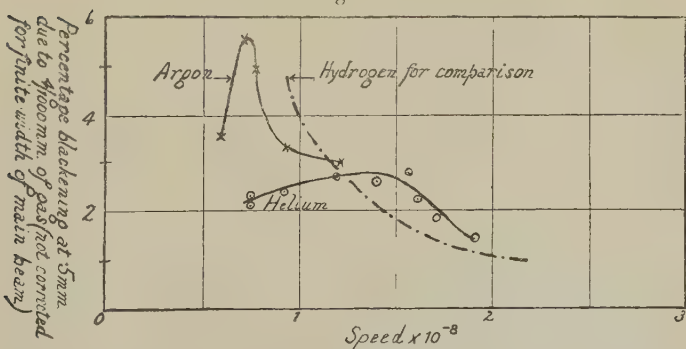


Fig. 2.



that the scattering should ever decrease with decreasing speed of the rays, but it will be remembered that Ramsauer and others have found an analogous effect in studying the absorption of slow electrons by gases. They observed that the absorption was a maximum for a certain speed, and

decreased for smaller speeds. It is of importance that these speeds are of the same order as those found in the present experiments, though of course the energies were much less, owing to the smaller mass of the electrons. Thus with argon Ramsauer found a maximum at 2.1×10^8 against $.75 \times 10^8$ in the present experiment, and with helium one at 1.35×10^8 against 1.4×10^8 . Further, in both experiments the maximum for argon is a sharp one and that for helium flat.

Collision Relation.

It is theoretically possible to calculate, from a knowledge of the density of the scattered radiation at various distances from the main beam, the chance that a ray shall be deviated through a given angle by a collision with a gas molecule. If there are N molecules per c.c. in the gas, we may write the chance of a collision as $N\psi(\theta)d\theta dx$ for a deviation between θ and $\theta + d\theta$ in the element of path dx . In the actual experiment the deflexions occur throughout the whole length of the scattering chamber, and are equally in all directions, while only the components perpendicular to the plane of the beam are observed. This has the effect of, as it were, blurring the features of the function ψ , so that its precise form cannot be determined with certainty. However, the general rate of change of number scattered with angle can be determined with some accuracy, so that if it is assumed that $\psi(\theta)$ is a power of θ , say $A\theta^{-n}$, the values of n and A can be found. This seems to be the best way of expressing the results of the experiments; but it must be emphasised that the form assumed for ψ is arbitrary, and probably almost any functional form which gave the same average rate of variation over the range of angles considered would fit the experiments almost as well. Once, however, a power law is assumed, n can be found with tolerable accuracy. The following is an outline of the method by which A and n can be determined.

For collisions occurring in a small element dx of the path of a ray, the chance of a collision between θ and $\theta + d\theta$ is $AN\theta^{-n}d\theta dx$. The surface density of the scattered particles on unit sphere with centre at dx is proportional to $AN/2\pi\theta^{n+1}$. In these experiments it is only scattering perpendicular to the slit which matters, and if ϕ is the projection of θ in this direction (see fig. 3), the chance of a scattered ray lying between ϕ and $\phi + d\phi$ is

$$\frac{d\phi}{\pi} \int_0^{\frac{\pi}{2}} \frac{AN\phi \sec^2 \alpha d\alpha}{\phi^{n+1} \sec^{n+1} \alpha} = \frac{d\phi}{\phi^n} \cdot \frac{AN}{2\sqrt{\pi}} \cdot \frac{\Gamma(n/2)}{\Gamma(n/2 + 1/2)} = B\phi^{-n}d\phi,$$

say.

The rays may be regarded as diverging from the centre of the condenser, and scattering may occur before or after the limiting diaphragm is reached. The pressure was such that the chances of multiple scattering can be neglected, and the scattering is considered as equally likely to occur at all points of the path of the ray. It is obvious that the law as stated can only hold if θ exceeds a certain minimum, otherwise the chance of scattering is no longer small. In practice

Fig. 3.

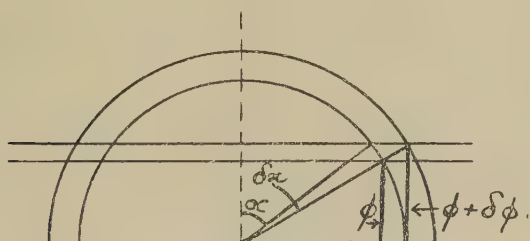
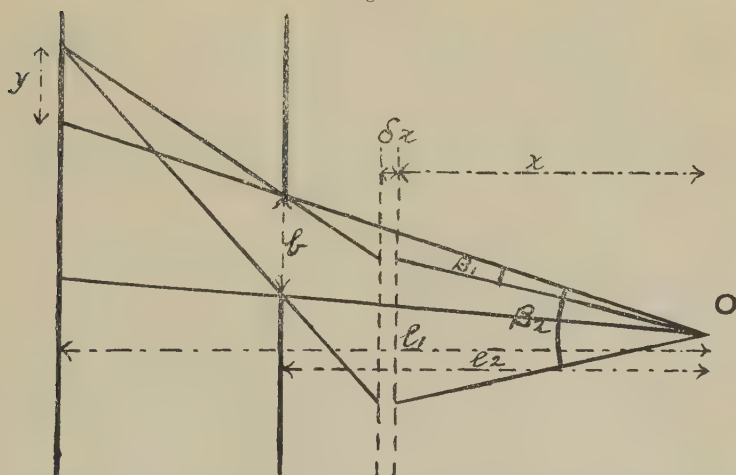


Fig. 4.



this is allowed for by only measuring the scattering some little distance from the edge of the main beam. (For a discussion of the conditions to be observed so that the combined effect of a number of small deflexions is negligible, see the previous paper.)

Let $Md\beta$ be the number of rays starting from O in the angle between β and $\beta + d\beta$ (see fig. 4). The value of ϕ for a ray to be scattered from a point (x, β) to a point on

the plate at a distance y from the edge of the main beam is $\phi = \frac{y + \beta l_1}{l_1 - x}$, the angles all being small.

The density at y due to scattering from $x d\beta dx$ will be

$$BM(l_1 - x)^{n-1}(y + \beta l_1)^{-n} dx d\beta.$$

The limits for β when $0 < x < l_2$ are β_1 and β_2 namely

$$y(l_2 - x)/x(l_1 - l_2) \quad \text{and} \quad \{y(l_2 - x) + b(l_1 - x)\}/x(l_1 - l_2).$$

When $l_2 < x < l_1$, the limits for β are 0 to b/l_2 . A straightforward integration gives for the total effect

$$\frac{BM(l_1 - l_2)^{n-1}}{n(n-1)} \left\{ \frac{1}{y^{n-1}} - \frac{1}{(y + 2a)^{n-1}} \right\},$$

where $2a = bl_1/l_2$, the width of the main beam at the plate. The density at y as a fraction of that of the main beam is thus

$$\frac{AN}{2\sqrt{\pi}} \cdot \frac{\Gamma(n/2)}{F(n/2 + 1/2)} \cdot \frac{l_1(l_1 - l_2)^{n-1}}{n \cdot (n-1)} \left\{ \frac{1}{y^{n-1}} - \frac{1}{(y + 2a)^{n-1}} \right\}^*.$$

From the observed variation of density with y , the best value of n was determined by trial and error, and A can then be found.

For both argon and helium, $n = 1.35$ was found to give the best fit at all speeds. Values of A are shown in the table. Fig. 2 shows the scattering at an arbitrary point

Table of Values of $A \times 10^{18}$ for Various Gases.

Velocity.	Argon.	Helium.	Hydrogen ($n=2$).
$\cdot 6 \times 10^{-8}$	6.5		
$\cdot 7$	10.2	4.0	
$\cdot 8$	6.9	4.3	
$\cdot 9$	6.3	4.5	1.75
1.0	5.9	4.8	1.40
1.2	5.6	5.1	1.05
1.4	5.2	.76
1.6	4.5	.56
1.8	3.2	.47
2.036

* *Correction.*—For the inverse square law of force $n=3$, and we have $\frac{AN}{24} l_1(l_1 - l_2)^2 \left\{ \frac{1}{y^2} - \frac{1}{(y + 2a)^2} \right\}$. On pp. 973-4 of the previous paper,

the factor $(l_1^3 - l_2^3)$ is given instead of $l_1(l_1 - l_2)^2$ in calculating the scattering to be expected on the inverse square law. The calculated figures on p. 974 are thus in error. As, however, the effect is to accentuate the differences between the observed and calculated values, the conclusion (that the inverse square law is inadequate) is not affected.

near the middle of the region studied, so as to make a rough comparison possible with hydrogen, for which n is different (approximately 2.0).

Oxygen.

Experiments had previously been made with oxygen. In this case it was necessary to have a stream of hydrogen flowing through the discharge-tube, and one of oxygen through the camera. Some mixing, of course, occurred through the slits in the cathode. This was allowed for approximately by measurements of the pressure when each stream was flowing separately, but the method is not very accurate. The amount of scattering, also, was too large for the scattering to be entirely "single." It could not be sufficiently reduced, as the amount of hydrogen present was fixed by the requirements of the discharge, and enough oxygen had to be present in the camera for its pressure to be comparable with that of the oxygen there. These difficulties might have been overcome by re-designing the apparatus, but it was felt that the preliminary results did not show sufficient points of interest to justify the expenditure of time, and that the inert gases were a more promising field. It was found, however, that the scattering per molecule in oxygen was much more than (about five times) that in hydrogen. The scattering seemed to increase with decreasing velocity throughout the range studied. The form of the collision relation was much the same as for the inert gases.

Discussion.

The most important point which emerges from these experiments is the analogy between scattering of protons and absorption of electrons shown by the occurrence of maxima at *velocities* of the same order (in the case of helium the velocities are the same within the experimental error). The natural explanation is some form of resonance effect, and it is important that the speeds are of the same order as those of the electrons in the outer Bohr orbits. The positive ray results are, however, much harder to explain on ordinary mechanics, because it is difficult to see how an electron moving in an orbit can produce much effect on a particle 1850 times its mass and moving with about the same speed. The angles of scattering observed are of the order .015, and from the conservation of momentum they can only occur if the atom moves as a whole to an appreciable extent. If the nucleus and electrons in the atom act separately on the ray according to the Coulomb law, or indeed any law of

the same general kind, the speed, or indeed the existence, of an electron can only matter if it is sufficiently firmly attached to the nucleus to be able to transfer a considerable amount of momentum to it.

The forces required to transfer this momentum are much larger than are usually supposed to be exerted on outer electrons. The inner electrons in argon would be expected to produce an appreciable effect; but their speeds are much greater than those of the rays, and so it is difficult to see how they can account for the maximum. It looks as though the atom must be regarded as a whole for the purposes of collisions of this kind, the periods associated with it being concerned with the whole mass and not merely with a particular electron. Alternatively one could suppose that the electrons are held rigidly in their orbits by some unknown forces. Dempster * has found that protons of about 900 volts pass through hydrogen and helium without becoming neutralized, and apparently without appreciable scattering. The method of experiment used by me is limited on the side of small velocities by the inefficient blackening produced. Indeed, I should probably not have been able to go so far as I did in the case of argon but for a batch of plates which was appreciably more sensitive to slow rays than those used for hydrogen.

It is hoped to continue the experiments on hydrogen, by another method, for slower speeds in order to see if there is a maximum in this case also.

My sincere thanks are due to the Department of Scientific Research for a grant towards the expenses of an assistant, Mr. J. D. McKay, to whose able help I am much indebted.

Summary.

The experiments are in continuation of those described in *Phil. Mag.* (May 1926). It is found that argon and helium show a maximum of scattering for a certain velocity of proton (0.75×10^8 and 1.4×10^8 respectively). This result appears to be analogous to those of Ramsauer and other workers with electrons of about the same speed, but is still more difficult to reconcile with the ordinary mechanical models of the atoms concerned. The experiments are consistent with a collision relation of the form $A\theta^{-1.35}$ in the case of both helium and argon, the index being independent of the speed. A few experiments on oxygen show large scattering but apparently no maximum.

Aberdeen, Sept. 1926.

* *Nat. Acad. Sci.* vol. xii. p. 96 (1926); *Nat. Acad. Sci.* vol. xi. p. 552 (1925).

XCIX. *The Activity Coefficients of Aqueous Hydrochloric Acid at Extreme Dilutions.* By GORDON NONHEBEL, B.A., B.Sc., Assistant Lecturer in Chemistry at the University of Leeds*.

THE present values of the activity coefficients of hydrochloric acid in aqueous solutions are based on the E.M.F. measurements of Linhart† and on the freezing-point measurements of Randall and Vanselow‡. In both cases an extrapolation of the experimental points to infinite dilution is necessary for the calculation of the activity coefficients, and for this reason some uncertainty still exists as to their true values. Owing to experimental difficulties, the data of Randall and Vanselow are somewhat irregular in the most dilute solutions, while the data of Linhart are not sufficiently numerous to admit of an unchallenged extrapolation.

Linhart measured the E.M.F. of cells $\text{H}_2/\text{HCl, aq.}/\text{AgCl:Ag}$ at 25°C. ; if M is the molality of the acid and γ the activity coefficient, then the observed electromotive force is given by

$$E = E_0 - 2 \frac{RT}{F} \ln M\gamma. \quad E_0 \text{ is a constant which is determined by extrapolation of the quantity } E_0' \left(= E + 2 \frac{RT}{F} \ln M \right) \text{ to}$$

infinite dilution, at which γ is, by definition, equal to unity. Linhart himself gave $E_0 = 0.2234$ volt, but his extrapolation was probably faulty, as he plotted E_0' against the logarithm of the concentration. Randall and Vanselow, by combining the activity coefficients calculated from their cryoscopic measurements with the E.M.F. data of Linhart in more concentrated solutions, found $E_0 = 0.2230$; and by a plot of Linhart's values for E_0' against the square root of the concentration found $E_0 = 0.2231$.

Debye's expression for the interionic forces in an aqueous solution of a uni-univalent electrolyte § leads to the limiting equation

$$-\log \gamma = 0.5 M^{\frac{1}{2}} \text{ at } 25^\circ.$$

Since

$$E_0' = E + 0.1183 \log M = E_0 - 0.1183 \log \gamma,$$

it follows that at extreme dilution E_0' should vary as $0.05915 M^{\frac{1}{2}}$. By making the curve $E_0'/M^{\frac{1}{2}}$ tangential to a

* Communicated by Dr. J. W. Nicholson, F.R.S.

† Journ. Amer. Chem. Soc. xli. pp. 1175 (1919).

‡ Loc. cit. xlv. p. 2418 (1924).

§ Physikal. Z. xxv. p. 97 (1924).

line of this slope 0.05915, Scatchard found $E_0 = 0.2226$ volt *, a method of extrapolation which is open to criticism. In a later paper † he has suggested that the value of E_0 might be lowered to 0.2224 in order to better the agreement between the experimental data and the complete Hückel equation ‡, in which account is also taken of the variation of the dielectric constant of the solution with the concentration. By plotting values of E_0 calculated from Milner's equation, of E_0 calculated from Debye's limiting equation, and of E_0' against the square root of the concentration, and by extrapolating the three curves to the same point, Nonhebel and Hartley § concluded that the most probable value of E_0 was 0.2229 ± 0.0001 volt.

In the work to be described, an attempt has been made to establish the value of E_0 for cells $H_2/HCl, aq./AgCl:Ag$ at 25° by the determination of sufficient experimental points to place the slope of the E_0' curve beyond doubt. Once E_0 is accurately known, reliable values for the activity coefficients may readily be calculated from the experimental data.

EXPERIMENTAL.

In view of the extreme dilution of the solutions, it is obvious that the slightest trace of impurity in the water may alter entirely their composition and properties. Uncertainty is also caused by possible adsorption of the acid on the electrodes, and by the necessity for a correction for the dissolved silver chloride, since in ten-thousandth molal solution this correction is as great as 0.6 millivolt.

Linhart used the precipitated form of silver chloride electrode. This attains equilibrium after a period which may be as long as three days, during which time the solution may easily become contaminated. Since calomel electrodes are completely unreliable in solutions of hydrochloric acid more dilute than 0.1 M, it was decided to use the electrolytic form of silver-chloride electrode which has been shown by Scatchard and by Nonhebel and Hartley (*loc. cit.*) to be reproducible to 0.1 mv. Such electrodes come to equilibrium rapidly, but will not maintain a constant potential in very dilute acid solutions for more than 36 hours.

In order to avoid contamination of the solutions by exposure to the atmosphere, a weighed amount of conductivity water

* Journ. Amer. Chem. Soc. xlvii. p. 641 (1925).

† *Loc. cit.* xlvii. p. 2098 (1925).

‡ *Physikal. Z.* xxvi. p. 93 (1925).

§ *Phil. Mag.* (6), i. p. 729 (1925).

was placed in the cell, and known quantities of a more concentrated solution of the acid added from a weight pipette. By making further additions when the cell had come to equilibrium, several concentrations could be studied with the same electrodes. The electrode vessel consisted of a "well-aged" Jena flask of 250 c.c. capacity, stoppered with a five-holed rubber bung. This carried the iridized gold hydrogen electrode, two silver-chloride electrodes, and a tube with a fine jet for the inlet of the hydrogen. A central tube, carrying the outlet bubbler on a ground over-cap, was used for the insertion of the weight pipette. The bubbler for saturating the incoming hydrogen with water-vapour was attached to the cell by means of a ground-joint, and was filled with conductivity water. The tubes carrying the electrodes etc. were of borosilicate glass. The rubber bungs were freed from uncombined sulphur by boiling in caustic-soda solution, washing with dilute acid and then with conductivity water.

The hydrogen and silver-chloride electrodes were freshly made for each run; they were prepared in the manner described by Nonhebel and Hartley for methyl-alcohol solutions, except that the silver-chloride electrodes were chloridized by electrolysis in an aqueous N/10 solution of the acid. After preparation, they were soaked in conductivity water for four hours before insertion in the cell. The hydrogen was generated by electrolysis of baryta; it was freed from spray by passage through a U tube packed with cellulose, and from traces of oxygen by passage over a hot tungsten filament. The freedom of the hydrogen from spray was proved by passing it through conductivity water for some time. The water used in these experiments had a conductivity of 0.5 reciprocal megohm; it was freed from dissolved air by evacuation in order to prevent the formation of air-bubbles on the electrodes and walls of the flask when the cell was placed in the thermostat. The solution of hydrochloric acid added from the weight pipette was approximately 0.07 N, and was standardized, through baryta, against constant boiling hydrochloric acid by weight titration. Owing to condensation of water in the tube leading to the exit bubbler, the concentration of the solution in the cell could not be known with an accuracy much greater than 0.2 per cent., corresponding with an error in E_0' of less than 0.1 mv.

The electrical apparatus was the same as that used by Nonhebel and Hartley. All the measurements were carried out at $25^\circ \pm 0.01^\circ$.

Experimental Procedure.—The Jena flask was dried and filled with a weighed amount of evacuated conductivity water. The electrodes, which were prepared the same day, were then mounted in the stopper, dried by touching their edges with filter paper, and inserted in the cell. Usually the cell was placed in the thermostat and the water saturated with hydrogen overnight; additions of acid were then commenced the following morning. The cells came to equilibrium within three hours of the first addition, but on further additions, equilibrium was reached within half an hour. A measurement was not accepted until the E.M.F. was constant for at least one hour. It was not found possible to make more than four additions in each run, as the electrodes then became sluggish and the silver-chloride electrodes often began to show discrepancies among themselves. An attempt was made to reach solutions of concentrations less than 0.0001 M, but experiments showed that at these dilutions the electrodes failed to come to equilibrium.

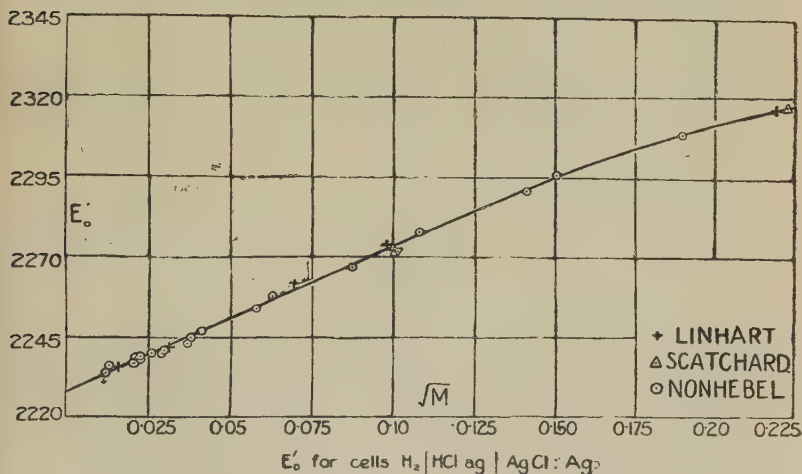
RESULTS.

All the observed E.M.F.'s have been corrected to a partial pressure of hydrogen of 760 mm. For the most dilute solutions correction also has been made for the solubility of the silver chloride in the manner described by Linhart. These corrected results, together with those obtained by Linhart and by Scatchard, are given in Table I. in order

TABLE I.

Series.	M.	E.	E_0' .	Series.	M.	E.	E_0' .
VI, i	0.0001182	0.6897	(0.2250)	II, iii	0.001705	0.5522	0.2247
Linhart	0.001360	.6805	.2231	IV, iii	0.01850	.5480	.2247
II, i	0.001529	.6748	.2234	II, iv	0.03377	.5178	.2254
IV, i	0.001602	.6726	.2236	III, ii	0.04006	.5094	.2258
Linhart	0.002420	.6514	.2236	Linhart	0.04826	.5002	.2262
II, ii	0.004185	.6233	.2237	VII, ii	0.07687	.4768	.2267
I, i	0.004381	.6210	.2237	Linhart	0.09650	.4658	.2274
V, i	0.004579	.6189	.2239	Scatchard ...	0.1002	.4638	.2273
Linhart	0.004830	.6161	.2238	„ ..	0.1010	.4633	.2272
IV, ii	0.005060	.6137	.2238	„ ...	0.1031	.4623	.2272
VI, ii	0.005071	.6137	.2239	III, iii	0.1166	.4565	.2278
I, ii	0.006793	.5987	.2240	III, iv	0.1970	.4309	.2291
III, i	0.008540	.5870	.2240	VII, iii	0.2263	.4242	.2296
V, ii	0.008915	.5849	.2241	VII, iv	0.3616	.4015	.2309
Linhart	0.01000	.5791	.2242	Linhart	0.4826	.3874	.2317
I, iii	0.01376	.5628	.2243	Scatchard ...	0.4986	.3858	.2318
VII, i	0.01467	.5597	.2245				

of ascending concentration, but the series in which the measurement was made is shown in the first column. Concentrations are expressed in gm. equivalents per 1000 gm. water. The figure shows a plot of E_0' against the square root of the molality: within the experimental error this curve is a straight line up to at least 0.005 M, and the points lie less well on the curve suggested by Scatchard*. The value of E_0 is therefore best calculated from the experimental data by the method of least squares, assuming that the



equation to the curve is $E_0' = E_0 + \sigma \sqrt{M}$. If this equation is true, then the activity coefficients are given by $-\log \gamma = A \sqrt{M}$, where the coefficient A is equal to $\sigma/0.1183$. Values of E_0 and of A calculated in this manner from the experimental data are given in Table II.

TABLE II.

Concn. range to zero ...	0.001	0.002	0.005	0.012 M
E_0 (volts)	0.2228 ₆	0.2228 ₇	0.2227 ₆	0.2228 ₀
A	0.35 ₁	0.35 ₆	0.39 ₆	0.38 ₂

It was deemed inadvisable to weight any of the points, though the first two in a run were possibly the more reliable. The most probable value of E_0 appears to be 0.2228 ± 0.0001 volt, in fair agreement with the value 0.2226 volt obtained by Scatchard by extrapolation of

* Journ. Amer. Chem. Soc. xlvii. p. 641 (1925).

Linhart's data. It is to be noted, however, that in his extrapolation Scatchard has made the line concave to the concentration axis in order to accommodate the point obtained by Linhart at the highest dilution measured, namely 0.000136 M. This does not seem to be justifiable in view of Linhart's belief that the point was unreliable and probably too low in value.

The most probable value of A is 0.39. According to the theory of Debye, $-\log \gamma = 0.505 \sqrt{M} - BM$, but up to 0.001 M the term BM may be neglected without appreciable error. Milner's calculation, on the other hand, leads to the equation $-\log \gamma = 0.37 \sqrt{M}$ approximately*, which agrees fairly well with the value 0.39 obtained experimentally. It seems evident, therefore, that for aqueous hydrochloric acid, as for its solutions in methyl alcohol †, the theory of Debye, while predicting correctly the general shape of the activity-concentration curve, gives too great a value for the slope A ‡.

SUMMARY.

The E.M.F. of cells $H_2/HCl\text{ aq.}/AgCl:Ag$ have been measured over a range of concentration extending from 0.00015 M to 0.04 M.

A new method of procedure for the measurement of these cells has been described.

The results indicate that the activity coefficient-concentration curve up to 0.005 M is given by the equation $-\log \gamma = A \sqrt{M}$, in which the constant A is equal to 0.39, a value somewhat smaller than that demanded by the equation of Debye for the interionic attraction in a strong electrolyte.

The author's thanks are due to Mr. D. M. Murray-Rust for carrying out two of the runs independently, to the Department of Scientific and Industrial Research for a maintenance grant, and to General H. B. Hartley, F.R.S., for valuable advice and encouragement during the progress of the investigation. The experimental part of this work was done at the Balliol and Trinity College Laboratory, Oxford.

August 1926

* See Nonhebel and Hartley, *loc. cit.*

† See, however, Scatchard, *Phil. Mag.* (7), ii. p. 577 (1926).¹

‡ In this connexion, see Pike and Nonhebel, *Phil. Mag.* 1. p. 723 (1925).

C. *On the Oblique Rebound of a Ball from a Fixed Plane.*
By R. C. J. HOWLAND, M.A., M.Sc., *University College, London*, and T. W. DICKSON, B.A., *City and Guilds (Engineering) College, London* *.

SUMMARY.

A BALL was dropped on to a fixed inclined plane, describing a trajectory after rebound. From direct observation of the path the nature of the rebound was deduced. As a result the usually accepted law of rebound is shown to be false, and an alternative law is suggested.

Introductory.

THE usually accepted laws of rebound may be summarized as follows :—

(1) The relative velocity normal to the surfaces at their point of instantaneous contact is reversed in direction and reduced in a ratio e . This ratio, generally called the coefficient of restitution, is a constant for the bodies concerned.

(2) The tangential impulse will be just sufficient to destroy the relative tangential velocity of the points in instantaneous contact unless the impulse required for this exceeds a certain limit.

(3) This limit is reached when the ratio of the tangential impulse to the normal impulse is equal to the coefficient of statical friction between the surfaces.

(4) When the tangential impulse needed to annul the relative tangential velocity exceeds this limit, the relative velocity is no longer destroyed : the ratio of the impulses remains at its limiting value.

For a ball striking a fixed plane, it is a consequence of these laws that the tangents of the angles of incidence and reflexion are proportional to one another for values of the angles below certain critical values, and are linearly related for larger values of the angles. The existence of these linear relations was confirmed in a series of rather rough observations by Mr. H. G. Green †. It is evident, however, that the truth of the laws cannot be inferred from these relations.

* Communicated by Prof. S. Chapman, D.Sc., F.R.S.

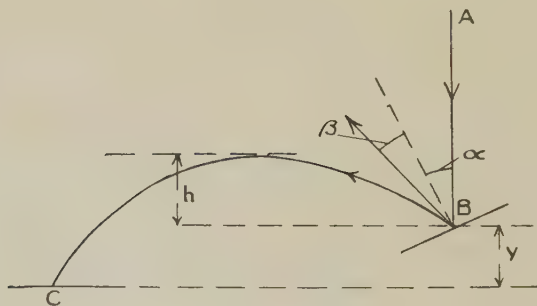
† "On a Method of Measurement of Newton's Coefficient of Restitution and the Law of Oblique Impact." *Phil. Mag.* 1, pp. 187-194 (1925).

In some experiments undertaken for a different purpose, Mr. L. Hock observed the trajectories of balls dropped vertically and rebounding from an inclined plane*. The range on a horizontal plane was measured, and also, in some cases, the angle of rebound. The results are compared by Mr. Hock only with the simplified theory in which the ball is treated as a particle. This naturally leads to a large discrepancy. It was, however, noticed by the present writers that, even when the theory is properly applied, a discrepancy remains. This is particularly noticeable in the angles of rebound. The angles observed indicate that the tangential impulse on the ball is considerably *greater* than that predicted by the theory. This unexpected result suggested that more refined experiments would be of interest. They were accordingly undertaken in the following manner.

Mode of Experiment.

The ball was dropped from a height on to a fixed inclined plane and allowed to rebound freely. It fell on a board

Fig. 1.



covered with white paper overlaid with carbon paper, so that the range was automatically recorded. Simultaneously, the trajectory was observed end-on with a cathetometer. It was found that a very clear sight of the ball at the top of its path could be obtained and the greatest height of the trajectory thus measured.

The ball being dropped from A (fig. 1) falls through a

* "Beiträge zur Prüfung des elastischen Verhaltens von Kautschuk, Stahl und anderen Stoffen," *Zeit. f. tech. Phys.* 1925.

height H and, striking the plane at B , rebounds to C , at a depth y below B . Then writing

height of top of path above $B = h$,
 vertical velocity before impact $= V$,
 „ „ after „ $= v$,
 horizontal velocity after „ $= u$,
 normal velocity towards plane before impact $= N$,
 „ „ away from plane after „ $= n$,
 tangential velocity down the plane before impact $= T$.
 „ „ „ „ after „ $= t$,
 „ „ of striking point of ball
 immediately after contact $= \tau$,
 horizontal range $= R$,
 initial angular velocity of ball after impact $= \omega$,
 radius of ball $= r$,
 angle of incidence $= \alpha$,
 „ rebound $= \beta$,

we have, neglecting air resistance,

$$V = (2gH)^{\frac{1}{2}}, \quad v = (2gh)^{\frac{1}{2}}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$u = \frac{R}{2y}(\sqrt{v^2 + 2gy} - v), \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$N = V \cos \alpha, \quad T = V \sin \alpha, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$n = v \cos \alpha + u \sin \alpha, \quad t = u \cos \alpha - v \sin \alpha, \quad . \quad (4)$$

$$e = n/N, \quad f = t/T, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$r\omega = 5(T - t)/2, \quad \tau = r\omega - t, \quad . \quad . \quad . \quad . \quad (6)$$

$$\tan \beta = t/n. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The nature of the rebound can thus be fully deduced from measurements of H , h , R , y , and α .

Apparatus and Materials.

Most of the observations were made with small balls of case-hardened steel of the type used for ball-bearings. The plane, of steel or glass, was bolted to a heavy anvil whose face could be clamped at any required angle to the horizontal. Initial attempts with a plane of fairly soft steel showed that a ball of $\frac{3}{8}$ in. diameter falling from a height of about 50 cm. indented the surface considerably. This increased the

resilience of the plane, and the ranges recorded in successive trials showed a systematic increase, sometimes up to 50 per cent. above the first observed. With a $\frac{1}{4}$ in. ball this effect was still too great to allow of successful experiments. This trouble was never wholly got over while a steel plane was used, but fairly satisfactory results were obtained with a plane of hardened silver-steel.

The best results were obtained with a sheet of plate glass. A $\frac{1}{4}$ in. ball, falling through about 60 cm., could be allowed to drop five or six times on the same spot before the surface of the glass was much injured. This gave ample time to align the cathetometer with the top of the path.

It was, of course, important that the ball should drop without initial spin. For this purpose, electromagnetic and pneumatic releases were tried and found unsatisfactory. Finally a mechanical release was used. This consisted of a short brass bar, pivoted at one end about a horizontal axis and held in a horizontal position by a catch. When the catch was released the bar was pulled down by a spring, the initial acceleration of the free end being greater than g . The ball, previously supported in an indentation at this end, was thus left in mid-air and fell freely without spin. The satisfactory working of this release was confirmed by the consistency of the results obtained.

All the vertical measurements were made with the cathetometer. The angle of the plane was taken with a clinometer.

Experiments were also made with a golf ball falling from a height of 7 ft. on to a heavy iron plate.

Results with $\frac{1}{4}$ in. Steel Ball on Glass Plane.

The measurements made are recorded in Table I. From these the values of N , T , n , t , e , f are found from equations (1) to (5). These are shown in Table II. In Table III. will be found the values of τ , $\tan \alpha$, $\tan \beta$, and $(T-t)/(N-n)$. This last measures the ratio of the tangential to the normal impulse. It should be noted that, according to the accepted theory, τ should be zero for all small values of α .

The upper limits to the experimental errors in the measurements of Table I. may be stated as 1 mm. in each of H , h , and y ; 2 mm. in R ; 5' in α . Most of the errors were certainly much less than these, especially for the larger values of α . From equations (1) to (6) may be found the maximum possible errors in e , f , and τ . These are shown, for three values of α , in Table IV.

TABLE I.

α .	H cm.	h cm.	y cm.	R cm.
0° 0'	60.1	49.7	—	—
4 45	60.4	49.0	13.5	29.3
9 40	61.1	46.2	27.7	60.5
14 30	61.0	41.0	27.8	83.4
19 45	61.1	33.8	27.7	101.9
24 40	61.2	25.4	27.5	113.5
29 35	61.7	15.6	27.0	119.3
34 50	61.2	7.4	27.5	110.7
39 40	61.0	1.9	27.8	95.2

TABLE II.

α .	N.	T.	n .	t .	e .	f .
0° 0'	—	—	—	—	0.910	—
4 45	343	28.5	313	17.6	0.912	0.62
9 40	341	58.0	311	35.4	0.913	0.62
14 30	335	86.6	306	50.7	0.915	0.59
19 45	326	117	298	68.6	0.916	0.59
24 40	315	144.5	288	92.3	0.916	0.64
29 35	302	172	277	132.5	0.915	0.77
34 50	285	198	261	164	0.917	0.83
39 40	266	221	244	197	0.918	0.89

TABLE III.

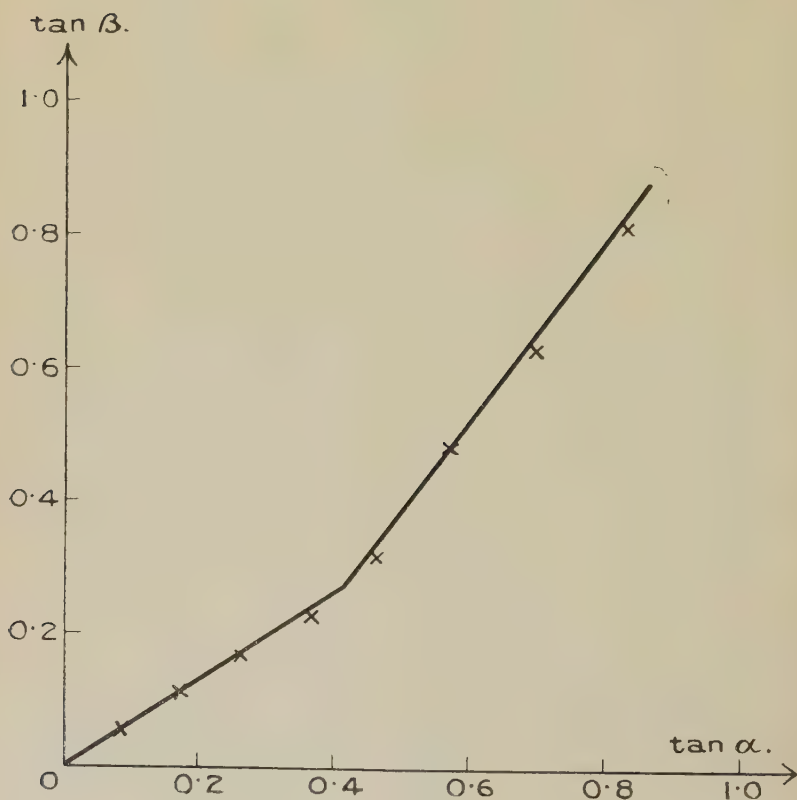
α .	τ .	$\tan \alpha$.	$\tan \beta$.	$(T-t)/(N+n)$.
4° 45'	9	0.083	0.056	0.017
9 40	21	0.170	0.114	0.035
14 30	39	0.259	0.166	0.056
19 45	52	0.359	0.230	0.078
24 40	38	0.459	0.321	0.087
29 35	-34	0.568	0.479	0.068
34 50	-80	0.696	0.630	0.062
39 40	-139	0.829	0.808	0.046

TABLE IV.

α .	Error in e .	Error in f .	Error in τ .
9° 40'	± 0.002	± 0.021	± 4.5
19 45	± 0.003	± 0.012	± 5.3
29 35	± 0.004	± 0.012	± 7.2

The regularity of the results for e indicates that the actual errors are considerably less than the limiting values here shown. But even if the errors are as great as these, the main conclusions are not affected.

Fig. 2.



Relations between the Angles of Incidence and Rebound.

In fig. 2 the relation between $\tan \alpha$ and $\tan \beta$ is shown graphically. It will be seen that, although the conditions of the ordinary theory are violated, the relations predicted by it are verified. This is especially remarkable in view of the figures given in the last column of Table III. It there appears that the ratio of the tangential to the normal impulse

increases with α until a critical value is reached, after which it shows a marked decrease. The maximum occurs at a point corresponding with the break in the graph in fig. 2. At this point slipping begins, and the lowest point of the ball moves forward after contact.

A determination of the coefficient of statical friction between the glass plate and the steel balls was made, the value obtained being 0.9. This corresponds closely with the greatest value of the ratio of the tangential and normal impulses.

Conclusions.

All the main features of the results given above were again observed in the experiments with other materials, with the exception that the drop in the ratio of the impulses after slipping occurred was less marked. The values of h and y showed a greater variation about the mean, and the final results were a little less regular, but they confirm the results for steel on glass in every particular.

The following statements may therefore be made with confidence :—

(1) Of the ordinarily accepted laws of rebound as stated in the introductory paragraph only the first is fully verified. e may be regarded as practically constant, but it increases slightly as the angle of incidence increases.

(2) The existence of a critical angle at which the law of rebound alters is also verified. This appears to happen when the ratio of the tangential to the normal impulse is slightly less than the coefficient of statical friction for the surfaces.

(3) For angles less than the critical angle the tangential impulse is much more than sufficient to bring the striking point of the ball to instantaneous rest. This point comes off the plane with a considerable *backwards* velocity.

(4) Before the critical angle is reached, the law is much more nearly expressed by the constancy of f , the ratio of the tangential velocity of the centre of the ball immediately after impact to that immediately before.

(5) For angles above the critical angle the ratio of the tangential to the normal impulse falls below the maximum value which it attains at the critical angle.

(6) The angles of incidence and rebound satisfy equations of the form

$$\begin{aligned} \tan \alpha &= a \tan \beta, & \text{for } \alpha < \alpha_0; \\ \tan \alpha &= b \tan \alpha - c, & \text{for } \alpha > \alpha_0. \end{aligned}$$

If a , b , c , be regarded as constants to be determined by experiment for each kind of material and surface, these equations, combined with the constancy of e , may be regarded as giving the laws of rebound.

For angles less than the critical angle, constancy of e and f might be taken as an approximate law. It is possible that in this form the law may extend to impacts in which both bodies are in motion. Experiments on such impacts would be interesting, but are very difficult to carry out effectively.

We are indebted to Assistant Professor H. Klugh for permission to perform the above experiments in the Mechanics Laboratory of the City and Guilds (Engineering) College.

CI. *General Formulæ for Two Syntonized Coupled Circuits.*
By RAYMOND M. WILMOTTE, B.A.*

MUCH has been written on the subject of coupled circuits. There is, however, a connexion between a balanced four-armed bridge and two syntonized coupled circuits, which, as far as I am aware, has not been pointed out. This similarity permits the general formulæ for tuned syntonized coupled circuits being obtained from the equivalent capacity and inductance of the coupled circuits. From this the general conditions for the coupled circuits having only one resonant frequency can be readily obtained.

1. *General Case.*

Consider the four-armed bridge (fig. 1). Suppose the impedances Z_1 , Z_2 , Z_3 , Z_4 are made up of resistances R_1 , R_2 , R_3 , R_4 in series with reactances X_1 , X_2 , X_3 , X_4 respectively. Then no current will flow in Z_0 when

$$Z_1/Z_4 = Z_2/Z_3. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Now, direct coupling between two circuits can be divided into three categories, in which the common reactance to both circuits is either in series with each circuit (as Z_0 in fig. 2), or in parallel to each circuit (as Z_0'), or a combination of both.

Fig. 2 can be redrawn as in fig. 3. The reactances X_1 , X_2 , X_3 , X_4 of DC, DB, CE, BE are $L_1\omega$, $-1/C_1\omega$, $L_2\omega$, $-1/C_2\omega$ respectively, where $\omega/2\pi$ is the frequency.

* Communicated by the Author.

Fig. 1.

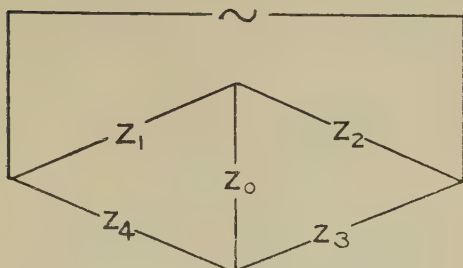


Fig. 2.

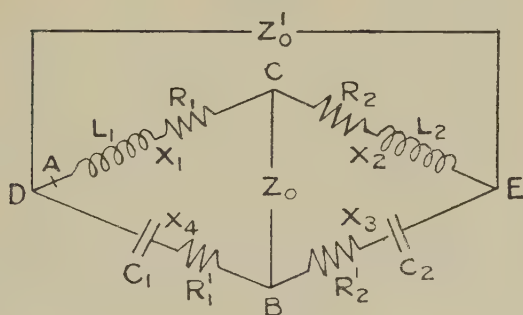
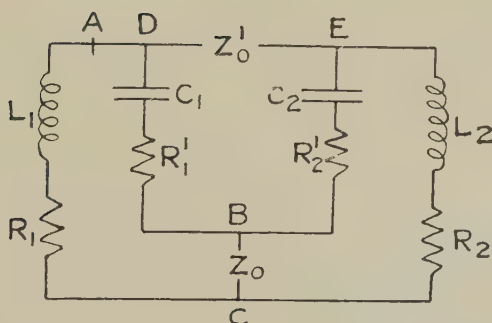


Fig. 3.



When the two circuits are syntonized, that is $L_1 C_1 = L_2 C_2$, we have

$$X_1/X_4 = X_2/X_3.$$

If at the same time

$$R_1/R_4 = R_2/R_3, \quad . \quad . \quad . \quad . \quad . \quad (2)$$

the equation is equivalent to equation (1).

Hence, if R_1 and R_2 are small and can be neglected compared with $L_1\omega$ and $L_2\omega$, as is usually the case, the coupled circuits become equivalent to a balanced four-armed bridge irrespective of condition (2). Hence, an E.M.F. across BC will produce no current in DE. This would be accurately so if the resistances R_1' and R_2' of the condensers C_1 and C_2 were connected by the relation

$$R_1'/R_1 = R_2'/R_2. \quad . \quad . \quad . \quad . \quad (3)$$

Suppose an E.M.F. be applied across BC. Let I_a be the current at any point A in the primary circuit produced by this E.M.F., the reactance of the coupled circuits referred to the point A being X_a . Since no current flows in Z_0' , X_a will be independent of Z_0' . Then the reactive power is $I_a^2 X_a$. Similarly, let I_b be the current at A when an E.M.F. is applied across DE, X_b being the reactance of the coupled circuits measured at A. In this case no current flows through Z_0 , so that X_b will be independent of Z_0 . The reactive power in this case is $I_b^2 X_b$. Now, since I_a is independent of I_b , the reactive powers can be added arithmetically.

If the current and equivalent reactance at A, when E.M.F.'s are applied simultaneously to BC and DE, are I and X respectively, we have, by equating the reactive powers,

$$W \equiv I^2 X = I_a^2 X_a + I_b^2 X_b. \quad . \quad . \quad . \quad . \quad (4)$$

Also it is evident that

$$I = I_a + I_b, \quad . \quad . \quad . \quad . \quad (5)$$

so that W is a minimum when

$$I_a X_a = I_b X_b.$$

Hence

$$X = \frac{X_a X_b}{X_a + X_b}. \quad . \quad . \quad . \quad . \quad (6)$$

This could have been obtained *a priori*, for the equations (4) and (5) are the same as those for two reactances X_a and X_b in parallel.

From equation (6) we have that at resonance, that is when $X=0$, either

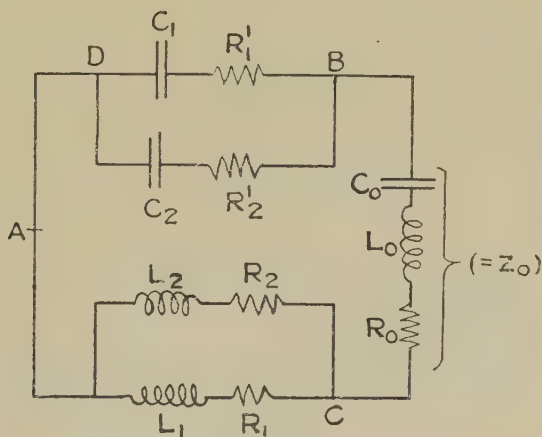
$$X_a=0 \quad \text{or} \quad X_b=0. \quad . \quad . \quad . \quad . \quad (7)$$

From this we see that at resonance, if an E.M.F. be applied at A, the current will be zero in either Z_0 or Z_0' , and resonance can occur at two states, when $X_a=0$ and $X_b=0$, for X will then be zero. We shall see that X_a and X_b can be readily obtained for these conditions.

Let us first consider X_a . For this case the points D and

E are at the same potential and the circuit can be redrawn as in fig. 4. The most general case is obtained by putting a self-inductance L_0 , a capacity C_0 , and a resistance R_0 all in series for Z_0 .

Fig. 4.



If we assume the resistances to be small compared with the reactances, with which they are connected in series, we can write immediately from the circuit the equivalent self-inductance, capacity, resistance, etc. of the coupled circuit, thus :—

$$\begin{aligned} \text{Equivalent self-inductance} \equiv L_a &= \frac{1}{\frac{1}{L_1} + \frac{1}{L_2}} + L_0 \\ &= \frac{L_1 L_2 + L_1 L_0 + L_2 L_0}{L_1 + L_2}. \quad (8) \end{aligned}$$

$$\begin{aligned} \text{Equivalent capacity} \equiv C_a &= \frac{1}{\frac{1}{C_1 + C_2} + \frac{1}{C_0}} \\ &= \frac{(C_1 + C_2) C_0}{C_1 + C_2 + C_0}. \quad \dots \quad (9) \end{aligned}$$

Hence

$$\begin{aligned} \text{Resonant frequency} &\equiv \frac{1}{2\pi \sqrt{L_a C_a}} \\ &= \frac{1}{2\pi \sqrt{\frac{[LC + L_0(C_1 + C_2)] C_0}{C_1 + C_2 + C_0}}}. \quad (10) \end{aligned}$$

In which, as before,

$$L_1 C_1 = L_2 C_2 = LC.$$

If the current in L_1 and C_1 is I_1 , and that in L_2 and C_2 is I_2 , then from fig. 4 it is evident that

$$I_1/I_2 = C_1/C_2, \quad \dots \quad (11)$$

and the current in Z_0 is $(I_1 + I_2)$.

The power dissipated is therefore

$$I_1^2(R_1 + R_1') + I_2^2(R_2 + R_2') + (I_1 + I_2)^2 R_0.$$

Hence the Equivalent resistance $\equiv R_a$

$$= \frac{(R_1 + R_1' + R_0)C_2^2 + (R_2 + R_2' + R_0)C_1^2 + 2C_1 C_2 R_0}{C_2^2}. \quad (12)$$

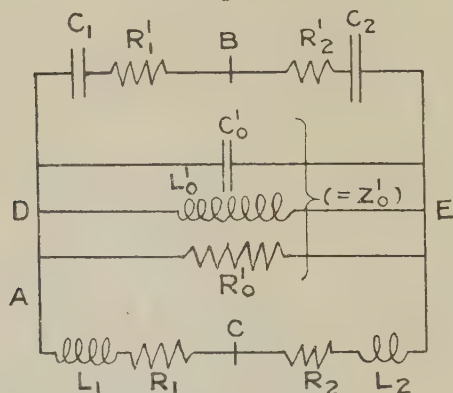
and

$$\text{Equivalent logarithmic decrement} = \frac{R_a}{2L_a n}, \quad \dots \quad (13)$$

where n is the frequency.

Treating X_b in the same way, we obtain fig. 5. Calling L_b , C_b , and R_b the equivalent self-inductance, capacity, and resistance respectively, measured at A of the coupled

Fig. 5.



circuits, when no current flows through Z_0 , we have for the most general case, in which Z_0' is made up of an inductance L_0' , a capacity C_0' , and a resistance R_0' (which is usually large compared with Z_0'), all in parallel,

$$\begin{aligned} L_b &= \frac{1}{\frac{1}{L_1 + L_2} + \frac{1}{L_0'}} \\ &= \frac{(L_1 + L_2)L_0'}{L_1 + L_2 + L_0'}; \quad \dots \quad (14) \end{aligned}$$

$$C_b = \frac{1}{\frac{1}{C_1} + \frac{1}{C_2}} + C_0' \\ = \frac{C_1 C_2 + C_1 C_0' + C_2 C_0'}{C_1 + C_2} \dots \dots \dots (15)$$

$$\text{Resonant frequency} \equiv \frac{1}{2\pi \sqrt{L_b \cdot C_b}} \\ = 2\pi \frac{1}{\sqrt{\frac{LC \cdot L_0'}{L_1 + L_2 + L_0'} \left[1 + \frac{C_0'}{C_1} + \frac{C_0'}{C_2} \right]}}.$$

If I_1' is the current in L_1 and L_2 , and I_2' is the current in C_1 and C_2 ,

$$I_1'/I_2' = 1/LC\omega^2. \dots \dots \dots (17)$$

Inserting the value for the resonant frequency, this becomes

$$I_1'/I_2' = L_0' \left(1 + \frac{C_0'}{C_1} + \frac{C_0'}{C_2} \right) / (L_1 + L_2 + L_0'). \dots (18)$$

Also the current I_0' in R_0' is given by

$$I_0' = I_1' \frac{(L_1 + L_2)\omega}{R_0'}.$$

Hence the power dissipated is

$$I_1'^2(R_1' + R_2') + I_2'^2(R_1 + R_2) + R_0' I_0'^2,$$

from which we have

$$R_b = R_1 + R_2 + \frac{R_1' + R_2'}{L^2 C^2 \omega^4} + \frac{(L_1 + L_2)^2 \omega^2}{R_0'}, \dots (19)$$

$$\text{and the equivalent logarithmic decrement} = \frac{R_b}{2L_b \cdot n}. \dots (20)$$

For the general case of fig. 2 there are two possible sets of constants for the resonant frequency. One is given by L_a , C_a , R_a , etc. of equations (1) to (13), and the other by L_b , C_b , R_b , etc. of equations (14) to (20). From these equations any case of direct coupling can be calculated at the resonant frequencies, if the following conditions hold :

$$R_1/R_1' = R_2/R_2'$$

and

$$L_1 C_1 = L_2 C_2 \equiv LC.$$

The first condition seldom holds, but this does not invalidate the theory, which will apply very approximately, if the resistances are small compared with their corresponding reactances, as is almost invariably the case.

TABLE I.

No.	Circuit.	Conditions	Inductance.	Capacity.	Resistance.	Logarithmic Decrement.	Resonant Frequency.
1	a	$C_0 = \infty$	$\frac{L_1 L_2 + L_1 L_0 + L_2 L_0}{L_1 + L_2}$	$C_1 + C_2$	$R_1 + R_2 \left(\frac{C_1^2}{C_2^2} + \frac{C_1 + C_2}{C_2} \right) R_0$	$\frac{R_1 L_1^2 + R_2 L_2^2 + R_0 (L_1 + L_2)^2}{2(L_1 L_2 + L_1 L_0 + L_2 L_0) \frac{L_1 + L_2}{L_1 L_2}}$	$\frac{1}{2\pi \sqrt{LC + L_0(C_1 + C_2)}}$
	b	$L_0' = \infty$ $C_0' = \infty$ $R_0' = \infty$	$L_1 + L_2$	$\frac{C_1 C_2}{C_1 + C_2}$	$R_1 + R_2$	$\frac{R_1 + R_2}{2(L_1 + L_2)n}$	$\frac{1}{2\pi \sqrt{LC}}$
2	a	$L_0 = 0$	$\frac{L_1 L_2}{L_1 + L_2}$	$\frac{(C_1 + C_2) C_0}{C_1 + C_2 + C_0}$	$R_1 + R_2 \left(\frac{C_1}{C_2} \right)^2$	$\frac{(R_1 L_1^2 + R_2 L_2^2)(L_1 + L_2)}{2 L_1^3 L_2 n}$	$\frac{1}{2\pi \sqrt{LC \cdot \frac{C_0}{C_1 + C_2 + C_0}}}$
	b	$L_0' = \infty$ $C_0' = \infty$ $R_0' = \infty$	$L_1 + L_2$	$\frac{C_1 C_2}{C_1 + C_2}$	$R_1 R_2$	$\frac{R_1 + R_2}{2(L_1 + L_2)n}$	$\frac{1}{2\pi \sqrt{LC}}$
3	a	$L_0 = 0$ $C_0 = \infty$ $R_0 = 0$	$\frac{L_1 L_2}{L_1 + L_2}$	$C_1 + C_2$	$R_1 + R_2 \left(\frac{C_1}{C_2} \right)^2$	$\frac{(R_1 L_1^2 + R_2 L_2^2)(L_1 + L_2)}{2 L_1^3 L_2 n}$	$\frac{1}{2\pi \sqrt{LC}}$
	b	$C_0' = 0$	$\frac{(L_1 + L_2) L_0'}{L_1 + L_2 + L_0'}$	$\frac{C_1 C_2}{C_1 + C_2}$	$R_1 + R_2 + \frac{(L_1 + L_2)^2 \omega^2}{R_0'}$	$\frac{R_0' (R_1 + R_2) (L_1 + L_2)^2 \omega^2}{2 R_0' (L_1 + L_2) \frac{L_1 + L_2}{L_1 L_2} + L_0'}$	$\frac{1}{2\pi \sqrt{LC \cdot \frac{L_0'}{L_1 + L_2 + L_0'}}}$
4	a	$L_0 = 0$ $C_0 = \infty$ $R_0 = 0$	$\frac{L_1 L_2}{L_1 + L_2}$	$C_1 + C_2$	$R_1 + R_2 \left(\frac{C_1}{C_2} \right)^2$	$\frac{(R_1 L_1^2 + R_2 L_2^2)(L_1 + L_2)}{2 L_1^3 L_2 n}$	$\frac{1}{2\pi \sqrt{LC}}$
	b	$L_0' = \infty$ $R_0' = \infty$	$L_1 + L_2$	$\frac{C_1 C_2 + C_1 C_0' + C_2 C_0'}{C_1 + C_2}$	$R_1 + R_2$	$\frac{R_1 + R_2}{2(L_1 + L_2)n}$	$\frac{1}{2\pi \sqrt{LC(1 + \frac{C_0'}{C_1} + \frac{C_0'}{C_2})}}$

In Table I. is given a list of special cases, in which the symbols are the same as have been used throughout. A point to be noticed in circuits 3 and 4 is that another impedance could be inserted between the points M and N; the effect on the formulæ would be to replace the coupling reactance by the sum of the two coupling reactances. Thus, if L_0'' and L_0''' were the coupling inductances in circuit 3, the formulæ would hold if $(L_0'' + L_0''')$ were substituted for L_0' . Similarly, for circuit 4 it would be necessary to write

$$\frac{C_0'' C_0'''}{C_0'' + C_0'''} \text{ for } C_0'.$$

2. Conditions for Single Frequency.

In certain cases using pure reactance coupling it is possible to obtain the condition that the two resonant frequencies are equal so that the circuit has apparently only one resonant frequency.

From equations (10) and (16) we see that the general condition for this to occur is given by

$$\frac{[LC + L_0(C_1 + C_2)]C_0}{C_1 + C_2 + C_0} = \frac{LC \cdot L_0'}{L_1 + L_2 + L_0'} \left[1 + \frac{C_0'}{C_1} + \frac{C_0'}{C_2} \right]. \quad (21)$$

In Table II. four special cases are given.

The peculiar property of circuit 5 of giving only one resonant frequency was first mentioned by Eccles and Makower in a paper to the British Association in 1915*. It will be seen that it is far from being the only case in which a single resonant frequency is obtainable when the resistances are small.

3. Limitations.

The method explained above only applies to forms of coupled circuits which can be represented by a balanced four-armed bridge. Thus, if circuit 1 of Table I. is adjusted so that

$$(L_0 + L_1)C_1 = (L_0 + L_2)C_2, \quad \dots \dots (22)$$

the method fails. This particular case is unfortunately of importance, for it is equivalent to the simple induction circuit.

In a straight induction circuit part of the lines of force link both circuits, and part (called the stray flux) link only one or other of the two circuits. If this stray flux produces

* 'Electrician,' vol. lxxv. p. 905 (1915).

TABLE II.

No.	Circuit.	Conditions.	Resonant Frequency.
5		$L_0 C_0 = LC$	$\frac{1}{2\pi\sqrt{LC}}$
6		$L_0' C_0' = LC$	$\frac{1}{2\pi\sqrt{LC}}$
7		$\frac{L_0'}{C_0} = \frac{LC}{C_1 C_2}$	$\frac{1}{2\pi\sqrt{LC \frac{L_0'}{L_1 + L_2 + L_0'}}$
8		$\frac{L_0}{C_0} = \frac{LC}{C_1 C_2}$	$\frac{1}{2\pi\sqrt{LC + L_0(C_1 + C_2)}}$

self-inductances L_1 and L_2 in the two circuits respectively, and the mutual inductance is M_0 , the circuits become evidently equivalent to circuit I, in which L_0 is replaced by M_0 . Usually, however, the circuits are syntonized according to condition (22). For this case, then, the method fails, but it would of course hold if the conditions were such that

$$(L_1' - M_0)C_1 = (L_2' - M_0)C_2,$$

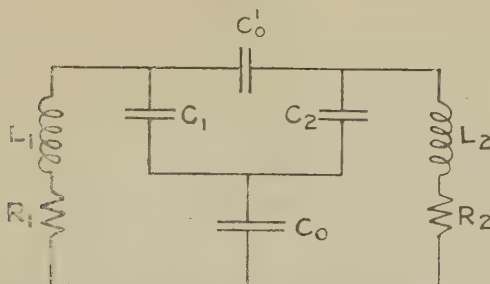
where L_1' and L_2' are the self-inductances of each circuit respectively when no current flows in the other.

4. *Experimental Verification.*

To test the theory experimentally a circuit, as shown in fig. 6, was set up. This was loosely coupled to an oscillator, and the current flowing in L_1 , L_2 and C_0' measured as the frequency was altered. The coupling remained unaltered, and it was ascertained that the current in the source remained very nearly constant over the range of frequency used. It was found, as expected, that near the higher resonant frequency the value of C_0' could be altered without

affecting the current in the parts of the circuit, and at resonance C_0' could actually be short-circuited without producing any appreciable effect. Near the lower resonant frequency the same was true with regard to C_0 .

Fig. 6.



Two such circuits, having constants given in Table III., were examined. The currents I_1 , I_2 , I_0 , I_0' in the inductances L_1 , L_2 and condensers C_0 , C_0' respectively were measured at the two resonant frequencies. The results are shown in Table IV., where they can be compared with the calculated values.

It will be seen that the agreement is well within the experimental error, when one considers that the frequency was about half a million and that the thermo-junction and

TABLE III.

(The opposite capacities are given in micromicrofarads.)

Circuit.	C_1 .	C_2 .	C_0 .	C_0' .	LC.
A.....	1000	2274	20000	50	0.112×10^{-12}
B.....	1195	500	5000	250	0.0592×10^{-12}

TABLE IV.

Circuit A.

	Higher Frequency.		Lower Frequency.	
	Observed.	Calculated.	Observed.	Calculated.
I_2/I_1	0.44	0.438	0.99	1.000
I_0/I_1	3.2	3.28	0	0
I_0'/I_1	0	0	0.08	0.067
Frequency ...	511,000	513,000	458,000	458,000

Circuit B.

	Higher Frequency.		Lower Frequency.	
	Observed.	Calculated.	Observed.	Calculated.
I_2/I_1	0.43	0.418	1.00	1.000
I_0/I_1	1.42	1.418	0	0
I_0'/I_1	0	0	0.42	0.415
Frequency ...	754,000	757,000	503,000	502,000

heater (of the non-contact type) had to be moved from one position in the circuit to another without altering the shape of the circuit in any way.

It was also found that, though the E.M.F. induced in the circuit was greater at the higher frequency, the value of I_1 was less. That is because the effective resistance at the higher frequency is greater than at the lower, as will be seen on examining Table I., the two cases that occur being 2 *a* and 2 *b*.

Circuit 8 (Table II.) was also set up and adjusted to give a single frequency. The constants of the circuit were as follows:— $C_1 = 1000 \mu\mu\text{F}$, $C_2 = 2830 \mu\mu\text{F}$, $C_0' = 470 \mu\mu\text{F}$, $L_0 = 11 \mu\text{H}$, $LC = 0.060 \times 10^{-12}$. The inductance L_0 was placed near the shield of a condenser, and it is probable that its effective value was appreciably decreased thereby.

As it was, the condition $L_0/C_0' = LC/C_1.C_2$ for a single frequency did not quite hold, for $L_0/C_0' = 0.023$ and $LC/C_1.C_2 = 0.021$. The agreement is not bad, but not perfect. By putting $L_0 = 10 \mu\text{H}$ perfect agreement would be obtained. The resonant frequency of this circuit was found to be 512,000, which compares well with the calculated value of 510,000.

4. *Conclusion.*

In conclusion, I would like to mention that for any given case it is probably easier to make use of the principle explained above for finding the equivalent constants of two syntonized coupled circuits at their resonant frequencies rather than substitute particular values in the somewhat cumbrous general expressions obtained. It will be found that for the cases to which the method applies it is much easier than the ordinary method of writing down the equations for the currents in the various branches of the net-work.

August 1925.

CII. *The Ranges of Secondary β -Rays.* By J. M. NUTTALL, M.Sc., Senior Lecturer in Physics, University of Manchester, and E. J. WILLIAMS, M.Sc., Fellow of the University of Wales*.

1. Introduction.

THE cloud method of photographing the tracks of ionizing particles, due to Professor C. T. R. Wilson, F.R.S., provides a means of determining the lengths of β -rays, free from difficulties arising from the scattering of the rays. The latter effect is very pronounced in the case of β -rays which have initial energies of the order of those of the rays produced by the photoelectric action of X-rays, and in other methods of making observations it is impossible to deal with the total distance traversed by these electrons. Theories of the decrease of velocity of electrons passing through matter deal with the total distance travelled, and it is important that this quantity should be observed. This is possible using Wilson's cloud method, since it records the actual path of the electron up to the point where it ceases to ionize the gas. This point can be taken as a convenient definition of the end of the ray, and the distance travelled up to this point as the range of the ray.

Previous measurements of the lengths of β -ray tracks, obtained by the cloud method, have been made by C. T. R. Wilson† and by H. Ikeuti‡. Wilson measured the ranges in air of the rays produced by the characteristic X-rays of copper and silver respectively, and Ikeuti determined the range in air of the rays produced by X-rays of wave-length 0.21 Å. The results obtained by these observers are in accordance with Whiddington's law which states that the range of a β -ray is proportional to the square of its initial energy. P. Auger§ has also made observations on the lengths of certain β -rays produced in a mixture of hydrogen and small quantities of the rare gases, in an investigation of the phenomenon of the production of "paired" β -rays, i.e., two rays having a common origin. In the theory of this phenomenon one of the two rays is assumed to be produced by the absorption of a quantum of the primary X-rays, and the other (called the "tertiary ray") by the absorption of the quantum of fluorescent X-rays subsequently emitted by the same atom. Auger finds that the relative

* Communicated by Prof. W. L. Bragg, F.R.S.

† C. T. R. Wilson, Proc. Roy. Soc. A, civ. p. 1 (1923).

‡ H. Ikeuti, *Comptes Rendus*, clxxx. p. 1257 (1925).

§ P. Auger, *Journal de Physique*, vi. No. 6, p. 205 (1925).

values of the ranges of the tertiary rays produced in different rare gases can be satisfactorily explained on the above-mentioned theory of their origin provided Whiddington's law holds. In the work of Wilson and Auger the β -rays measured are produced by fluorescent X-radiations. The K and L radiations of an element differ in wave-length by about 15 per cent., and therefore produce β -rays possessing initial energies differing to the same extent, and this makes an accurate interpretation of the results obtained in such cases difficult. Again, in all the experiments referred to the β -rays are produced in gaseous mixtures, which means that there will be further inequalities in the initial energies due to the different ionization potentials of the constituent elements.

In the present experiments simple gases have been used as far as possible, and the β -rays have been produced by homogeneous X-rays reflected from a crystal. Observations have been made on the β -rays produced in oxygen, nitrogen, hydrogen, and argon by X-rays of wave-lengths ranging from 0.41 Å to 1.54 Å. The results obtained and described in this paper show how the range of β -rays in a given gas varies with the initial energy of the rays, and also how the range depends on the nature of the gas.

2. Experimental Method.

The experimental arrangement used for the production and photographing of the β -rays has been fully described in a previous paper* by the authors on " β -rays associated with scattered X-rays," and it is only necessary here to point out that in all the experiments homogeneous X-rays, obtained by reflexion from a crystal, were used to produce the β -rays, and that in all cases stereoscopic photographs were taken in order that measurement of the lengths of the β -ray tracks in space might be made. The lengths of the tracks were obtained from the stereoscopic photographs by replacing the photographic plates in the camera, illuminating them, and tracing out the common image, which coincides in space with the original track provided the adjustment of the camera is exactly the same as when the photographs were taken.

3. Initial Energies of the β -rays.

The initial energy, E , of the β -rays produced by the photoelectric action of radiation of frequency ν is given by Einstein's photoelectric equation

$$E = h\nu - \epsilon,$$

* Nuttall & Williams, Phil. Mag. i. p. 1217 (1926).

ϵ being the energy lost by the photoelectron in escaping from the atom. It is almost impossible in the cases of oxygen, nitrogen, and argon to ascertain from the β -ray track the energy-level in the atom from which the photoelectron is ejected. The value of ϵ , even for the most firmly bound electrons, is, however, in all these cases small compared with the energies of the X-ray quanta concerned, and a sufficiently accurate value of the effective binding energy can be deduced from the following considerations. The magnitude of the discontinuity in the absorption of X-rays by an element as the wave-length of the X-rays passes the K absorption limit for that element, and the nature of the variation of the absorption with wave-length on either side of the limit, indicate that for radiation of wave-length less than that corresponding to the K absorption limit, the absorption by the K electrons is about $6/7$ ths of the total absorption. The magnitude of the L discontinuity shows that the greater part of the remaining absorption is due to the L electrons. As ϵ is small compared with $h\nu$, its effective value can therefore be taken as $(6/7\epsilon_K + 1/7\epsilon_L)$, where ϵ_K and ϵ_L are the binding energies of the K and L electrons respectively. This is the effective value of ϵ used in calculating the initial energies of the β -rays, equation (1) becoming

$$E = h\nu - 6/7\epsilon_K - 1/7\epsilon_L. \quad . \quad . \quad . \quad (1a)$$

In the case of the β -rays produced in a mixture of hydrogen and a small quantity of argon the paired tracks, according to Auger *, consist of a β -ray ejected from the K level of argon and another ray due to the absorption by the same atom of the K fluorescent quantum subsequently emitted, which has a range of about 1 mm. Assuming the interpretation to be correct, we can distinguish the β -rays which originate in the K level of argon when argon is present in small quantities in an atmosphere of hydrogen. In the present experiments this has been done in the case of β -rays produced in such a mixture by X-rays of wave-length 1.54 \AA , the initial energy in volts of the rays considered being 4800, as compared with an average initial energy of 7560 volts for β -rays ejected from oxygen atoms by the same radiation. The difference is appreciable, and by measuring the length of these rays additional information can be obtained about the β -rays in hydrogen without using radiation of a different wave-length.

* *Loc. cit.*

4. *Range in Gaseous Mixtures.*

It can be readily shown that if the variation of range with initial energy obeys the same law in different gases $g_1, g_2 \dots g_n$, then the range r_m of a β -ray in a mixture of these gases is given by

$$\frac{1}{r_m} = \frac{p_1}{r_1} + \frac{p_2}{r_2} + \dots \frac{p_n}{r_n}, \quad . \quad . \quad . \quad (2)$$

where r_n is the range of the β -ray in the gas g_n when its pressure and temperature are the same as those of the mixture, and p_n is the partial pressure of the gas g_n in the mixture expressed as a fraction of the total pressure of the mixture.

In all experiments using the cloud method, water-vapour is essentially present in the cloud chamber where the β -rays are produced, and the correction necessary in order to obtain the range in the pure gas concerned has been made by applying equation (2). In the cases of oxygen, nitrogen, and argon this correction is very small, being in no case greater than 1 per cent. In the case of hydrogen it is more appreciable, being of the order of 10 per cent. The condition of application of equation (2) is in all cases considered to be sufficiently well satisfied to ensure corrections of the necessary accuracy.

5. *Results.*

The results obtained in the present experiments are shown in Table I.

Column 1 gives the nature of the gas in the cloud chamber, column 2 the wave-length of the X-rays used to produce the secondary β -rays, and column 3 the number of β -ray tracks measured in each case.

The initial energy of the β -rays, calculated from equation (1 a), is given in column 4 and is stated in *volts* (V). Column 5 gives the mean range (in cm.) of the β -rays at 0° C. and 76 cm. pressure. It might be pointed out here that the ranges of the separate β -ray tracks for any given initial energy vary between fairly wide limits (± 30 per cent. of the mean value), but that in taking a series of measurements the mean value is only altered by very small amounts after about eight tracks have been examined. In most cases about twenty tracks were measured, and in general it was found that the shorter tracks were those of β -rays which had suffered most deflexions. The 6th column gives the value of R/V^2 in each case, and column 7 gives the mean value of R/V^2 for a given gas.

TABLE I.

Gas.	Wave-length of exciting X- rays in \AA .	No. of tracks examined.	Initial energy of β -rays expressed in volts (V).	Mean range of β -rays in cm. at N.T.P. (R).	$R_v \times 10^9$.	Mean values of $R_v \times 10^9$.	Atomic stopping- power of gas.	Atomic No. of gas.
Oxygen O_2 ...	1.54	35	7,560	.101	1.76)			
"709	15	16,910	.49	1.71)			
"614	19	19,590	.67	1.76)	1.75	(8)	8
"545	22	22,130	.87	1.78)			
Nitrogen N_2	.614	19	19,700	.77	1.98)			
"	.545	22	22,240	1.01	2.05)	2.01	7.0	7
Argon A_1614	20	17,220	.48	1.62)			
"545	20	16,760	.65	1.66)	1.63	17.0	18
"41	6	27,190	1.20	1.62)			
Hydrogen H_2	1.54	20	7,560	.73	12.71)			
"	1.54	15	4,800	.35	15.63)	14.2	1.0	1

6. *The Variation of Range with the Initial Energy of the β -ray.*

According to Whiddington* the range of a β -ray is proportional to the square of its energy or, in terms of our foregoing nomenclature, $R \propto V^2$. The results given in column 6 of Table I. show that this law holds with a high degree of accuracy for β -rays produced by X-rays of wave-lengths $\cdot 41$ – $1\cdot 54$ Å in oxygen, nitrogen, and argon. The initial energies of these β -rays range from 7,560 to 27,190 volts and in the case of oxygen, for instance, the results cover a nine-fold variation of the range of the rays. The slight deviation in the two values of R/V^2 in the case of hydrogen may be due to uncertainty in the calculation of V , the initial energy of the rays, since here the values of the binding energies of the ejected electrons are of more relative importance than in the other cases, and this is especially so in the case of the rays for which V is estimated as 4,800.

7. *Variation of Range of β -rays with Nature of the Gas.*

It is seen from column 7 of the Table (which gives the mean values of R/V^2 for a given gas) that the range of a β -ray of given initial energy varies with the nature of the gas in which it has been observed, being greater the lower the atomic number of the gas. The mean value of R/V^2 gives a measure of the reciprocal of the molecular stopping power of the gas. In order to obtain the atomic stopping power we must take into account the monatomic or diatomic nature of the gas. The stopping powers per atom for the different gases are given in column 8 of the Table, the value for oxygen being arbitrarily chosen as (8). The mean stopping powers of the atoms of nitrogen, argon, and hydrogen then become 7, 17, and 1 respectively. Thus the relative atomic stopping powers of the gases are approximately proportional to their atomic numbers or to the number of extra-nuclear electrons per atom, as given in the last column. We may therefore conclude that R is proportional to $\frac{1}{N}$, where N is the atomic number of the gas and R is the range in the gas at a given atomic concentration, of β -rays of given initial energy.

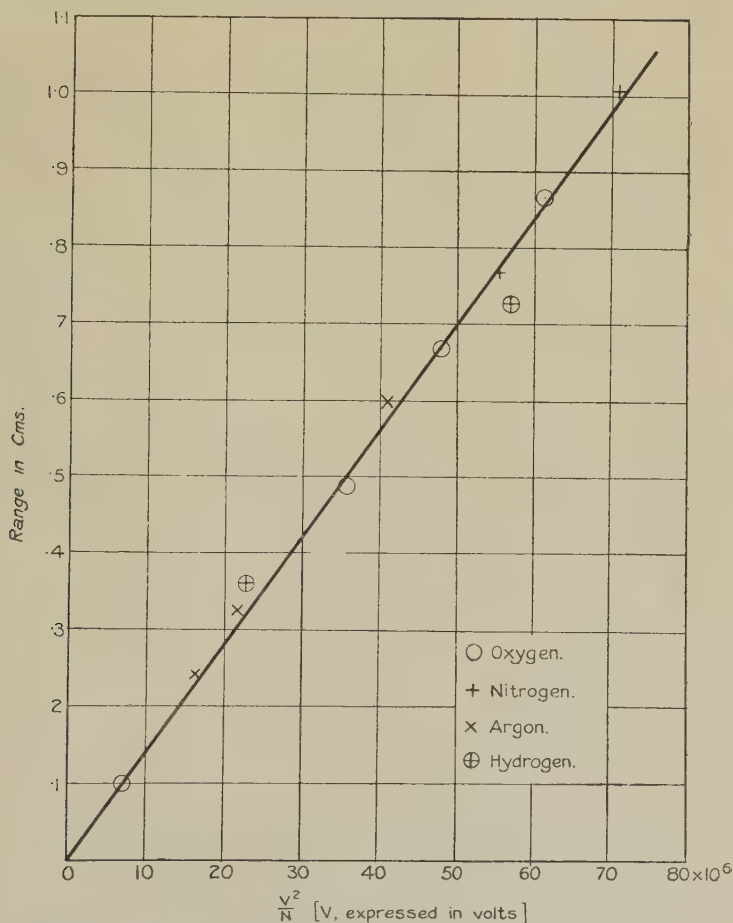
The two laws connecting the range of the secondary β -rays with initial energy and atomic number of the gas traversed

* R. Whiddington, Proc. Roy. Soc. A, lxxxvi. p. 360 (1912).

respectively can be expressed by the relation

$$R = K \frac{V^2}{N},$$

where K is a constant and R is the range in the gas at a given *atomic* concentration. For an atomic concentration equal to that in a diatomic gas at N.T.P. the numerical value of K which represents the present results is 1.42×10^{-8} .



The extent to which the ranges of the β -rays produced in the different cases investigated in the present work obey this law can be realized from the figure. The values of R for the

gas at atomic concentration equal to that of a diatomic gas at N.T.P. is plotted along the axis of abscissæ and the value of V^2/N along the axis of ordinates. If the law was accurately obeyed all the points would lie on a straight line through the origin. The straight line drawn corresponds to the value of K given above.

The theoretical significance of the results described in this paper are being considered and it is hoped to publish an account of the results in the near future.

8. Summary.

The Wilson cloud method has been used to photograph the tracks of secondary β -rays produced by a beam of homogeneous X-rays of known wave-length in the gases oxygen, nitrogen, argon, and hydrogen. The stereoscopic photographs of the β -ray tracks have been examined and measured and the ranges of the β -rays at N.T.P. deduced.

It is found that for any one gas, the range of the β -ray is proportional to the square of its initial energy (Whiddington's law), the agreement holding over a range of energies from 4,800–27,190 volts. It is also found that the range of the β -ray varies as the reciprocal of the atomic number of the gas, for equal atomic concentrations. Both these relations are included in the law expressed by $R = KV^2/N$, K being a constant and having the value 1.42×10^{-8} when R is the range in a gas at atomic concentration equal to that of a diatomic gas at N.T.P.

In conclusion the authors desire to express their thanks to Professor W. L. Bragg, F.R.S., for his interest and helpful suggestions during the progress of the work.

Physical Laboratories,
Manchester University.
August 1926.

(CIII. *Notes on Scattered X-Rays. The J Phenomenon* (Part V.). By Prof. C. G. BARKLA, F.R.S., and GLADYS I. MACKENZIE, M.A., B.Sc., University of Edinburgh*.

IN an earlier paper † we described two alternative ways in which the beams of X-rays scattered in directions making angles at 60° and 120° with the primary radiation differed

* Communicated by the Authors.

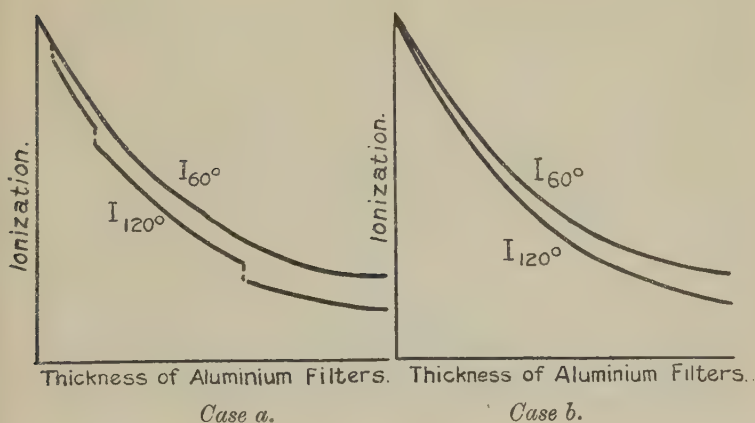
† "Notes on the Superposition of X-rays and on Scattering. The J Phenomenon (Part III.)." *Phil. Mag.* Feb. 1926.

from one another. In one case the beam at 120° was absorbed at the same rate as the beam at 60° ; but the intensity of the former, as measured by ionization in a short electroscope, dropped suddenly when the heterogeneous beam by filtering reached certain critical penetrating powers. These were the J_1, J_2, J_3 discontinuities shown by the radiation scattered at 120° and not by that scattered at 60° .

In the other case the beam at 120° appeared continuously more absorbable than that at 60° , giving the superficial appearance of the Compton difference of wave-length with angle of scattering.

In the one case, *Case a*, as the beams were transmitted through aluminium, and by filtering reached higher and higher *average* frequencies, there appeared three strongly-marked "absorption lines" in the beam at 120° , but not in the beam at 60° . In the other case, *Case b*, instead of showing "absorption lines" the beam at 120° was continuously more absorbable than that at 60° . It was already in the region beyond an "absorption edge."

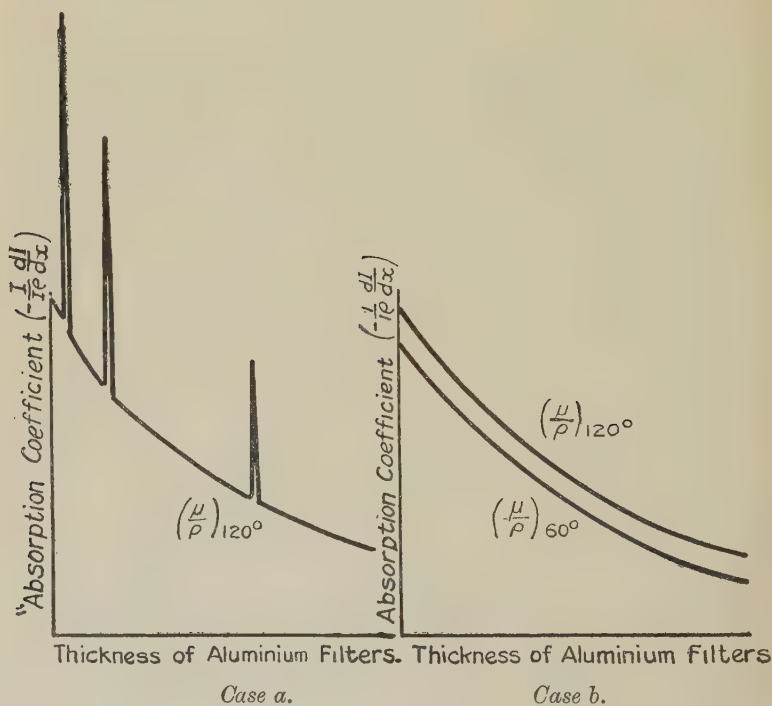
Fig. 1.



These results are indicated in figs. 1 and 2. In fig. 1 ionization is plotted against thickness of intercepting aluminium; I_{120° showing the steps, I_{60° showing steadily decreasing intensity in *Case a*. In the alternative case, *Case b* (Exper. 13 in previous paper), neither beam showed any discontinuity by successive filtering, but I_{120° fell more rapidly than I_{60° , that is the former was more absorbable.

In fig. 2 absorption-coefficients [or more accurately $-\frac{1}{I\rho} \frac{dI}{dx}$, where I is the ionization] are plotted against the thickness of aluminium, the beam at 120° showing the peaks, but that at 60° giving a smooth curve in *Case a*. The other case is shown on the right side of the figure with no unusual features, but the beam at 120° has a steadily higher "absorption-coefficient."

Fig. 2.



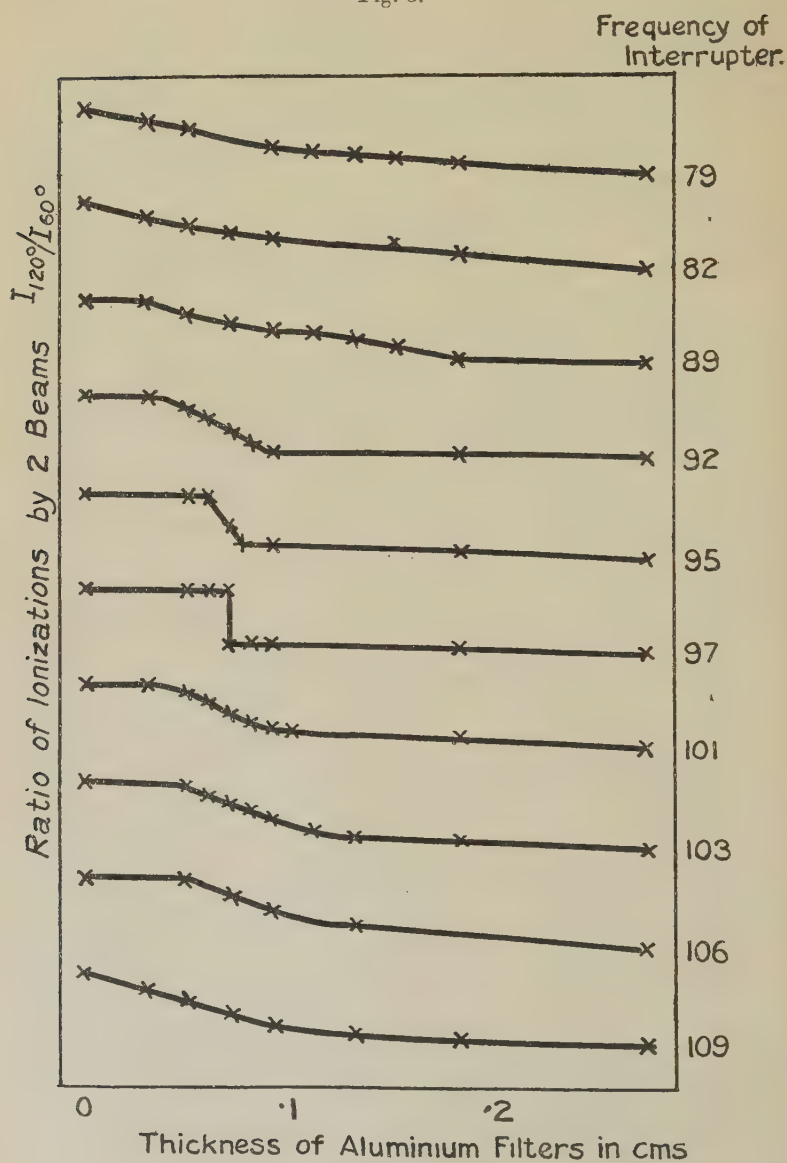
At the time of these experiments there was no indication of the cause of the difference between the two results, or of the factors which determined whether the result of the experiment should be (a) or (b). It had, however, been made clear that these were of a nature never previously taken into consideration, and that the distinctive feature was the dependence on some sort of average constitution of the whole heterogeneous beam, and not on any particular

constituent frequency, or even simple combination of frequencies. A systematic search of the cause of the variable result showed at once that it depended on the details of the process of excitation of the X-rays. The X-ray tube was excited by an induction coil with mercury jet interrupter. The frequency of interruption of the primary current was varied, and experiments were performed in the manner previously described. It was seen that *Case a*, showing discontinuities, gradually merged into *Case b*, showing a steady difference of absorbability as the frequency of interruption was changed. More precisely *Case a*, showing very abrupt discontinuities, was produced at only a very definite frequency of interruption, or over a very narrow range of frequencies; with lower and higher frequencies the width of the "absorption line" increased rapidly until it spread through the whole of the absorbability spectrum, and *Case a* had become *Case b*. Thus fig. 3 gives the ratio of $I_{120^\circ}/I_{60^\circ}$ for various thicknesses of absorbing aluminium and for frequencies of interruption varying from 79 to 109 per second. At a frequency 97 per second the change in ionization was most abrupt.

Thus by change of frequency of the interrupter the "absorption lines" of fig. 2 become wider and less strongly marked absorption-bands, until the band covers the whole range of the absorbability spectrum, which is then *Case b* (fig. 2). *Case b* was thus connected up to *Case a* by a continuous series of results. The frequency of the interrupter is, of course, not the fundamental factor; indeed, with another X-ray tube the critical frequency was not 97 but considerably over 100. And later still, after many alterations, only *Case b* appeared throughout the whole range of frequencies, as is shown in fig. 4, obtained with the same tube. Cases *a* and *b* are only widely-separated forms of exactly the same phenomenon—a conclusion to which we were led by experiments of a different kind. Thus, again, what superficially appeared to support Compton's theory was shown to be no other than the J phenomenon appearing in the scattered radiation.

The further discussion of the conditions essential to the appearance of a discontinuity will be given later. Our main purpose at present is to record the fact that the factor which decides the degree of activity due to a complex beam acting as a whole is to be found in the details of the method of excitation of the X-rays; that is, it is determined by the large-scale structure of the radiation and not by its constituent frequencies. It might be expected that the more

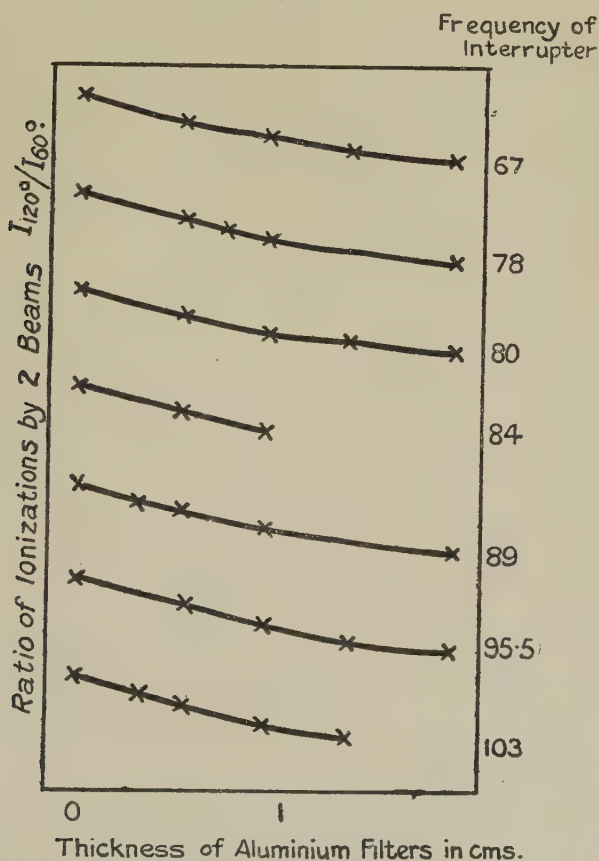
Fig. 3.



continuous (the less intermittent) is a stream of radiation, the higher is the degree of coherence it will show. And though the magnitudes considered as providing a sufficient

degree of homogeneity in the radiation are large compared with a wave-length, they are probably minute compared with those associated with a frequency of one hundred or thereabouts. But the material necessary for a profitable discussion of these questions has not yet been fully published.

Fig. 4.



It might be recorded that the variable factor appears to have been eliminated by Dr. W. H. Watson in this laboratory, working with an alternator-transformer and Coolidge tube. Results will shortly be published. The variations of potential supplied by a coil and interrupter are naturally much less regular than those from such an alternator-transformer.

CIV. *The Control of the J Phenomenon* (Part VI.). By Prof. C. G. BARKLA and Dr. W. H. WATSON, *University of Edinburgh* *.

THE conditions determining the nature and properties of a beam of X-rays have hitherto not been sufficiently under control to enable us to ensure the certain occurrence of the J discontinuities in the activity of the radiation studied. The apparently capricious nature of the phenomenon, when its occurrence under a wide variety of conditions was established, became not a subject for criticism, however, but one of its most significant and important features, for it indicated the influence of factors previously considered as of little moment.

The regularity of the phenomenon under suitable conditions enabled us to determine many of the laws which govern it. In many cases these suitable conditions were sufficiently persistent to ensure the repetition of the phenomenon week after week, and even month after month. Also the conditions of experiments undertaken in the laboratory by eight or nine experimenters over many years were sufficiently varied to show the general nature of the phenomenon. [Probably not more than 1/20th part of the experimental evidence has been recorded.]

In an attempt to obtain more complete control, it was, of course, essential to use a Coolidge tube. Such tubes had previously been employed, but not under the best conditions. In Dunbar's experiments †, for instance, in which an induction coil and mercury interrupter were used, the discontinuities certainly appeared, but the conditions were not sufficiently controllable, nor was the experiment itself of the kind which was later found most suitable to exhibit the phenomenon.

In other experiments with the Coolidge tube (conducted by Mr. Stevens: results unpublished) extensive series of observations showed the very precise difference in the levels of activity of a primary and of a scattered beam, exactly as with gas tubes away from the region of a discontinuity, showing that the same laws were operative with the Coolidge and gas tubes. But on only one occasion was there observed the change of activity in one beam such as characterizes a J discontinuity. The tube in this case also was worked by an induction coil and mercury interrupter. The only partial

* Communicated by the Authors.

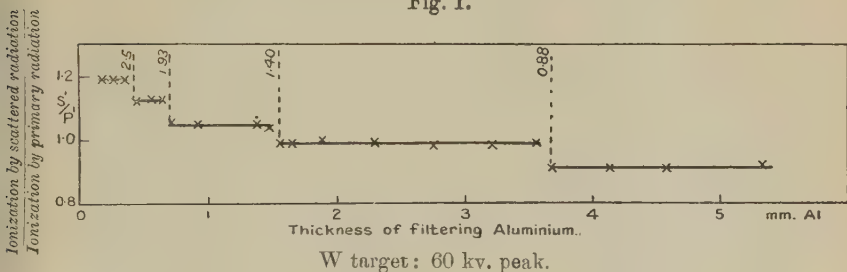
† Phil. Mag., January 1925.

success of the experiments with the Coolidge tube and induction coil with mercury interrupter led to our use of a rotary converter with transformer to supply the high potential.

By very careful regulation of the filament current in the Coolidge tube, and of the applied potential, some of the most interesting results have been obtained.

The experiment, in brief, was to compare the radiations scattered from a paraffin cylinder in the direction making an angle of 90° with the primary beam with the primary itself by the method of Barkla and Khastgir—*i. e.*, by placing successive equal thicknesses of aluminium in both beams and studying the ratio of the ionizations produced by these two in similar electroscopes. Typical results are shown in fig. 1, in which the ratio of ionizations by scattered and

Fig. 1.



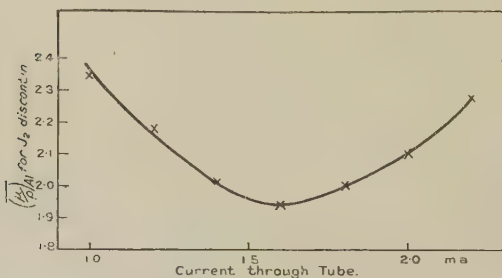
W target: 60 kv. peak.

primary radiations is plotted against thickness of filtering aluminium placed in the path of each. The constancy of this ratio, $\frac{\text{ionization by scattered radiation}}{\text{ionization by primary radiation}}$, for various thicknesses of aluminium shows the precisely equal absorptions of scattered and primary radiations between the J discontinuities. The discontinuities show the sudden changes in the ionization produced by the scattered radiation when by filtering this arrived at certain critical absorbabilities, or at any rate at certain average constitutions measured to a first degree of approximation by an average absorption-coefficient. These, of course, are the J discontinuities similar to those observed by Barkla and Khastgir in a comparison of the scattered with the primary X-radiation, and by Barkla and Gladys I. Mackenzie in the radiation scattered at 120° , when compared with that scattered at 60° with the primary.

The important features of these experiments are the following:—

- (1) By careful control it has been found possible to obtain consistent results throughout the whole series of experiments. The J discontinuities have been observed without exception in every experiment; they appear to be under perfect control.
- (2) New discontinuities have been observed between what have been previously called J_1 and J_2 and also between J_2 and J_3 . The second of these had, however, been observed in one or two experiments by Miss Mackenzie. In our experiments it occurred without exception.
- (3) In previous experiments the discontinuities had appeared at absorbabilities which, though calculated from a 50-per-cent. absorption, were remarkably constant. In these experiments a regular systematic variation of $\left(\frac{\mu}{\rho}\right)_{Al}$ (calculated from a 50-per-cent. absorption) has been obtained by varying the current

Fig. 2.



Mo target. 40 kv. peak.

through the Coolidge tube. Thus fig. 2 shows the relation between $\frac{\mu}{\rho}$ corresponding to the critical state for the J_2 discontinuities and the current through the tube in milliamperes. The critical absorbability, as previously measured, is thus appreciably dependent upon the total measure of the stream of electrons striking the anti-cathode. Such a dependence of the critical $\frac{\mu}{\rho}$ upon the current passing through the tube has been found for each of the discontinuities observed.

- (4) Further, in each case a relationship of the form shown in fig. 2 for the J_2 discontinuities has been found. In each case also the minimum value for $\frac{\mu}{\rho}$ corresponds very closely with the value which was found to be so constant in the experiments with gas-tubes and with a mercury break interrupter.

In our experiments these minimum values of $\left(\frac{\mu}{\rho}\right)_{Al}$ are 3.76, 3.24, 2.44, 1.94, 1.40, 0.73, 0.47,

corresponding to the values—

$$\begin{array}{ccccccc} J_1 & & J_2 & & J_3 & J_4 & J_5 \\ 3.8 & - & 1.9 & - & 0.7 & (0.47) & 0.34 \end{array}$$

previously published *.

That this variation in the critical value of $\frac{\mu}{\rho}$ was not due simply to variation in intensity of the radiation was shown by experiments at different distances from the anti-cathode. When the current through the tube was constant, the critical absorbability was independent of distance from the tube, and thus of simple intensity. The variations illustrated in fig. 2 are thus not fundamentally associated with intensity of radiation; they are dependent on a quality of the whole stream of radiation generated at the anti-cathode.

It should, however, be pointed out that the method of measuring the absorbability of a complex radiation, by taking a 50-per-cent. diminution of the ionization, is a quite arbitrary one. And our method of measuring the average constitution could not be expected to give the quantity defining the position of a J discontinuity with any precision. The remarkable feature has been that it has varied so little under great variety of conditions. This is partially explained

by the relationship illustrated in fig. 2, for the critical $\frac{\mu}{\rho}$ as previously published is really a minimum value, so there is little variation of its value over a wide range of current.

With a given current through the tube, a variation of potential applied to the tube of course changed the wavelength and general absorbability; but the critical absorbability for the discontinuity was not appreciably changed.

* "The J Phenomenon (Part I.)," Phil. Mag., May 1925.

Thus, when a lower potential was applied, the radiation was of lower frequency, softer, and thus had to be filtered by greater thicknesses of aluminium before the critical absorptability was reached—in agreement with previous experiments.

The only difference observed between the absorptabilities of scattered and of primary radiations throughout these experiments has been in the appearance of the J discontinuities (or absorption lines) in the progressive absorption of the scattered radiation. Thus the horizontal lines between the discontinuities of fig. 1 show the precisely equal absorptions of secondary and primary. Such relationship as that of fig. 1 has previously been shown by Barkla and Miss Mackenzie for secondary radiations scattered at angles of 120° and 60° . Barkla and Khastgir, however, usually found that beyond the discontinuity the scattered radiation was more absorbable than the primary, although it was equally absorbable before the occurrence of the discontinuity; that is, the discontinuity initiated a definite change in the level of absorptability of the secondary radiation. In our experiments the difference between the secondary and primary was shown only at the discontinuities. There was never any evidence of a difference in absorptability provided the discontinuities did not become blurred by the variation of conditions during the experiment.

As the position of a discontinuity measured as indicated depends on the current through the tube, it would be expected that under variable conditions these discontinuities would be spread out and would show an apparently steady higher absorption of the scattered than of the primary radiation, such as has frequently been found in experiments on the progressive absorption of both beams. This suggests that all the apparent differences between scattered and primary radiations as shown by some absorption experiments may be fundamentally made up of such discontinuities.

There is, of course, a vast field for research in the subject of the J phenomenon. We wish for the present only to record the advances made in these experiments, a fuller account of which will appear elsewhere.

Summary.

Control of the J discontinuities and associated phenomena has been obtained.

Further discontinuities have been found.

The critical absorbabilities (as usually measured) have been found to vary systematically with the current through the Coolidge tube.

In these controlled experiments no difference has been observed between the absorptions of primary and scattered radiations, except by the occurrence of the J discontinuities (or absorption lines) in the progressive absorption of the scattered radiation.

CV. *The Density of Fluids.*—I. *On a Relation between Density and Temperature and on the Latent Heat of Vaporization.* By J. H. SHAXBY, D.Sc., F.Inst.P., Physiology Institute, Cardiff*.

THE average value of the intermolecular distances in any fluid, or in other words the density of the fluid, must obviously be determined by a sort of balance between molecular attractions tending to greater condensation and molecular movements tending to wider dispersal. The following paper is a somewhat speculative attempt to give these general notions a greater precision.

Just as the relation of density to height in the case of an isothermal atmosphere is given by the equation

$$\rho = \rho_0 e^{-\frac{V}{RT}}, \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which ρ is the density at a height where the potential energy is V , and ρ_0 the density at datum level where the potential energy is zero, so we may suppose that the uniform density ρ of a fluid is given by an equation of the same form, where V now denotes the potential energy of intermolecular forces corresponding to the actual state of packing of the molecules, and ρ_0 is the density of close packing when this potential energy is zero. V is itself therefore a function of the density ρ , and the problem resolves itself into that of finding the form of that function.

To remove a molecule, initially in close proximity to a second, to an infinite distance in the absence of other molecules would require an amount of work E_0 , and in falling back the same amount of work would be done by the molecule. In the case of an actual fluid this process becomes

* Communicated by the Author.

less simple: other molecules intervene and disturb the returning one by their attractive forces and by collisions. Hence when a molecule, coming from infinity, does at last reach the second or "goal" molecule it brings with it a quantity of energy which is no longer E_0 . We may look at the matter in a rather different way by supposing the moving molecule to have reached a given stage in its journey, and considering its chances of continuing a stage further in the right direction without more than a permissible disturbance. Thus if a molecule P is at a given instant moving towards the "goal" molecule, its direction must lie within a cone of solid angle determined by the diameter of the molecules and its distance from its destination, the axis of the cone being the line joining the centres of the given molecules. Let us call the solid angle ω . The distribution of the remaining molecules may be supposed to possess a simplifying regularity, such that the molecules nearest P all lie on the surface of a sphere with its centre at P and of radius r equal to the average distance apart of molecules in the fluid of density ρ . The product ρr^3 is constant for any given fluid, so the area ωr^2 cut off on this spherical shell by the cone is inversely proportional to $\rho^{2/3}$, while the surface density of molecules in the shell is directly proportional to the same quantity. With closer packing, the chance of the molecule P coming within a given distance from another molecule is of course increased, but since all intermolecular distances are at the same time decreased P is moving, so to speak, in a "stiffer" field. The chance of a disturbance, measured by the angular deflexion of P's path, exceeding any specified amount is determined by the ratio of the distance of approach to the mean distance r . Thus for a given angular displacement the distance of approach must be reduced in the same proportion as r . So we may take as the measure of the disturbance the chance of the ratio of the distance of P from a second molecule on its passage through the shell to the distance r being less than some assigned value. This chance is proportional to the number of molecules of the shell in the area ωr^2 and is thus constant, whatever the packing.

This is otherwise obvious, since the number of molecules in the shell remains constant as the density increases, so that the chance of a molecule lying within the solid angle ω also remains unchanged. The chance of a given angular disturbance of P's motion is thus independent of the density of the fluid.

In traversing any given distance x , P has to run the gauntlet of such disturbance x/r times, and the total chance

of a given deviation is thus inversely proportional to r , in other words directly proportional to the cube root of the density. The chance of escaping such deviation is thus proportional to $1 - c\rho^{1/3}$, where c is a constant.

Hence, with a large number of molecules such as P , the fraction which succeeds in bringing its quota of energy E_0 to the goal molecule is $1 - c\rho^{1/3}$, so that the effective average energy is

$$E_0(1 - c\rho^{1/3}) = E_0 - B\rho^{1/3}.$$

We may conveniently deal with a gramme-molecule of the substance, so that the symbols E_0 , R , etc. refer to that quantity, *i. e.*, to 6.07×10^{23} molecules.

Thus, writing $B\rho^{1/3}$ for E_0 and $\alpha/3$ for R/B , we have

$$\rho = \rho_0 e^{-\frac{B(\rho_1^{1/3} - \rho^{1/3})}{RT}} = \rho_0 e^{-\frac{3(\rho_1^{1/3} - \rho^{1/3})}{\alpha T}}. \quad (2)$$

Hence

$$\rho_1^{1/3} - \rho^{1/3} = \frac{\alpha T}{3} (\log_e \rho_0 - \log_e \rho) = \alpha T (\log_e \rho_0^{1/3} - \log_e \rho^{1/3}), \quad (3)$$

or

$$\rho^{1/3} - \alpha T \log_e \rho^{1/3} = \rho_1^{1/3} - \alpha T \log_e \rho_0^{1/3}. \quad (4)$$

2. Applying these equations to a liquid and its saturated vapour both at absolute temperature T , and denoting their densities by ρ and σ respectively, we have

$$\rho^{1/3} - \sigma^{1/3} = \alpha T \log_e \left(\frac{\rho}{\sigma} \right)^{1/3}, \quad (5)$$

from which we can calculate the value of α . Table I. gives the result for a number of substances over wide ranges of temperature, the highest being in most cases the critical temperature. The data have been drawn from the values of ρ and σ given in the article on Vapour Pressures (L. Graetz) in Winkelmann's *Handbuch der Physik*, Kaye and Laby's Tables and *l'Annuaire du Bureau des Longitudes*.

The value of α at the critical temperature T_c is $\frac{\rho_c^3}{T_c}$, the limiting value of $\frac{\rho^{1/3} - \sigma^{1/3}}{T \log_e \left(\frac{\rho}{\sigma} \right)^{1/3}}$ when both ρ and σ become

equal to the critical density ρ_c .

It will be seen that the value of α is nearly independent

of temperature, at least for substances which are not associated in the liquid state. Values of f_0 and ρ_1 were determined by trial and the equation (4) above found to hold satisfactorily, but such methods of evaluating ρ_0 and ρ_1 are unnecessary, as will be shown, so their values are not inserted here.

TABLE I.

WATER.		MERCURY.		CARBON DISULPHIDE.	
Temp.° C.	$\alpha \times 10^3$.	Temp.° C.	$\alpha \times 10^3$.	Temp.° C.	$\alpha \times 10^3$.
0	2.07	180	2.88	-3.1	3.30
20	2.13	220	2.91	8.2	3.20
40	2.19	260	2.94	16.3	3.31
60	2.24	300	2.95	22.4	3.32
80	2.28	340	2.95	27.0	3.32
100	2.31	360	2.95	373	3.05
120	2.31			(Crit.)	
364.2	2.50				
(Crit.)					
AMMONIA.		CARBON DIOXIDE.		ISOPENTANE.	
Temp.° C.	$\alpha \times 10^3$.	Temp.° C.	$\alpha \times 10^3$.	Temp.° C.	$\alpha \times 10^3$.
0	3.43	0	5.75	20	3.05
20	3.45	10	5.75	60	3.06
40	3.46	30	5.82	100	3.04
60	3.44	30.5	5.83	140	3.02
80	3.42	31	5.84	180	3.04
100	3.39	31.35	5.86	186	3.05
132.9	3.51	(Crit.)		187.8	3.08
(Crit.)				(Crit.)	
ETHER.		PENTANE.		HEXANE.	
Temp.° C.	$\alpha \times 10^3$.	Temp.° C.	$\alpha \times 10^3$.	Temp.° C.	$\alpha \times 10^3$.
20	3.05	40	2.96	60	2.70
60	3.09	80	2.96	100	2.72
100	3.09	120	2.95	140	2.72
140	3.08	160	2.95	180	2.72
180	3.09	180	2.95	220	2.74
190	3.12	190	2.97	230	2.75
193.8	3.16	197.2	2.94	234.7	2.80
(Crit.)		(Crit.)		(Crit.)	

The values of α in Table I. are thus found by assuming that equation (4) holds equally for liquid and vapour, and the constancy of the resulting figures shows that this assumption is approximately true. But it appears desirable to explore the equation further, which we may do by taking the value of α at the critical temperature where there is no

distinction between liquid and vapour and inserting this value $\frac{\rho_c^{1/3}}{T_c}$ in equation (4). We thus have

$$\rho^{1/3} - \frac{\rho_c^{1/3} T}{T_c} \log_e \rho^{1/3} = \rho_1^{1/3} - \frac{\rho_c^{1/3} T}{T_c} \log_e \rho_0^{1/3}, \quad \dots \quad (6)$$

which at the critical temperature reduces to

$$\rho_c^{1/3}(1 - \log_e \rho_c^{1/3}) = \rho_1^{1/3} - \rho_c^{1/3} \log_e \rho_0^{1/3}. \quad \dots \quad (7)$$

Now at the critical temperature it is reasonable to suppose, as has often been done, that molecular kinetic and potential energies become equal. Thus $V_c = \frac{3}{2}RT_c$. Hence from equation (1)

$$\frac{\rho_c}{\rho_0} = e^{-3/2},$$

or

$$\rho_0^{1/3} = e^{1/2} \rho_c^{1/3}. \quad \dots \quad (8)$$

Substituting this value in (7),

$$\rho_c^{1/3}(1 - \log_e \rho_c^{1/3}) = \rho_1^{1/3} - \rho_c^{1/3}(\frac{1}{2} + \log_e \rho_c^{1/3})$$

$$\text{or} \quad \rho_1^{1/3} = \frac{3}{2} \rho_c^{1/3}. \quad \dots \quad (9)$$

We may thus rewrite equation (6) in the form

$$\rho^{1/3} - \frac{\rho_c^{1/3} T}{T_c} \log_e \rho^{1/3} = \frac{3}{2} \rho_c^{1/3} - \frac{\rho_c^{1/3} T}{T_c} \log_e (e^{1/2} \rho_c^{1/3}),$$

$$\text{i. e.} \quad \frac{\rho^{1/3}}{\rho_c^{1/3}} - \frac{T}{T_c} \log_e \frac{\rho^{1/3}}{\rho_c^{1/3}} = \frac{3}{2} - \frac{1}{2} \frac{T}{T_c}. \quad \dots \quad (10)$$

If we put $\frac{\rho^{1/3}}{\rho_c^{1/3}} = \phi$ and $T/T_c = \theta$, we obtain a "reduced" equation, containing no quantities specific to any particular substance :

$$\phi - \theta \log_e \phi = \frac{3 - \theta}{2}. \quad \dots \quad (11)$$

Further, $V = E_0 \left(1 - \frac{\rho^{1/3}}{\rho_1^{1/3}}\right)$, of which a special case is

$$V_c = E_0 \left(1 - \frac{\rho_c^{1/3}}{\rho_1^{1/3}}\right). \quad \text{But } V_c = \frac{3}{2}RT_c \quad \text{and} \quad \frac{\rho_c^{1/3}}{\rho_1^{1/3}} = \frac{2}{3}.$$

$$\text{Therefore} \quad \frac{3}{2}RT_c = \frac{1}{3}E_0, \quad \text{or} \quad E_0 = \frac{9}{2}RT_c. \quad \dots \quad (12)$$

Hence the characteristic molecular energy E_0 of a substance is numerically equal to three times the kinetic energy at the critical temperature. The critical temperature may thus be taken as a measure of this characteristic energy, the energy required to dissipate the substance from a state of close molecular packing to one of infinite separation of its molecules. Numerically, E_0 is $3.74T_c \times 10^8$ ergs or approximately $9T_c$ calories per gram-molecule, $6.17T_c \times 10^{-16}$ erg per single molecule.

3. The values of $\rho_0^{1/3}$, $\rho_1^{1/3}$, E_0 , and V_c , estimated from the experimental data for densities at different temperatures, are shown in Table II. together with the corresponding quantities $e^{1/2}\rho_c^{1/3}$, $\frac{3}{2}\rho_c^{1/3}$, $\frac{3}{2}RT_c$, and $\frac{3}{2}RT_c$, for a number of substances.

TABLE II.

Substance.	$\rho_0^{1/3}$.	$e^{1/2}\rho_c^{1/3}$.	$\rho_1^{1/3}$.	$\frac{3}{2}\rho_c^{1/3}$.	$\frac{\rho_0^{1/3}}{\rho_1^{1/3}}$.
Water	1.142	1.139	1.039	1.036	1.099
Mercury	2.692	—	2.447	—	1.091
Carbon					
disulphide ...	1.215	1.191	1.128	1.084	1.077
Ammonia	1.055	1.020	0.941	0.927	1.120
Ether	1.065	1.055	0.962	0.960	1.107
Isopentane	1.000	1.016	0.910	0.925	1.099
Heptane	1.038	1.016	0.931	0.925	1.114
Methyl					
propionate ...	1.135	1.119	1.022	1.018	1.111
Diisopropyl	1.001	1.010	0.920	0.932	1.088

Substance.	10 ¹⁰ ergs/gm. molec.			
	E_0 .	$\frac{3}{2}RT_c$.	V_c .	$\frac{3}{2}RT_c$.
Water	23.52	23.85	7.89	7.95
Mercury	—	—	—	—
Carbon				
disulphide...	19.06	20.43	6.85	6.81
Ammonia	15.40	15.19	5.28	5.06
Ether	17.20	17.47	5.75	5.82
Isopentane	17.18	17.24	5.46	5.75
Heptane	20.99	20.21	7.06	6.74
Methyl				
propionate...	20.46	19.85	6.78	6.62
Diisopropyl	18.17	18.73	5.90	6.24

The ratio of $\rho_0^{1/3}$ to $\rho_1^{1/3}$ is also given; as shown above this ratio should be $\frac{e^{1/2}}{3/2}$ or 1.099.

Table III. exhibits the general fit of equations (4) or (6). Examination of this table shows that the equations hold with a high degree of accuracy for liquids, but less closely for saturated vapours. The latter give a fair approximation at temperatures not too far from the critical, *i.e.* when the vapour density is great, but there are increasing divergences as the temperature falls.

TABLE III.

Temp. °C.	$\rho_1^{1/3} - \alpha T \log \rho_0^{1/3}$	$\rho^{1/3} - \alpha' T \log \rho^{1/3}$	$\sigma^{1/3} - \alpha T \log \sigma^{1/3}$
WATER ($\alpha = 2.496 \times 10^{-3}$, $\rho_1^{1/3} = 1.039$, $\rho_0^{1/3} = 1.142$).			
0	1.000	1.000	
60	0.992	0.996	
120	0.982	0.989	
364.3	0.947	0.946	
AMMONIA ($\alpha = 3.508 \times 10^{-3}$, $\rho_1^{1/3} = 0.93$, $\rho_0^{1/3} = 1.02$).			
0	0.9218	0.9234	1.008
40	0.9206	0.9207	0.9297
80	0.9194	0.9198	0.9322
132.9	0.9177	0.9158	
HEPTANE ($\alpha = 2.60 \times 10^{-3}$, $\rho_1^{1/3} = 0.925$, $\rho_0^{1/3} = 1.016$).			
80	0.9182	0.9189	0.9523
120	0.9175	0.9176	0.9378
160	0.9167	0.9165	0.9309
200	0.9159	0.9163	0.9282
240	0.9153	0.9161	0.9224
260	0.9148	0.9149	0.9164
264	0.9147	0.9142	0.9144
266.9	0.9147	0.9184	

TABLE IV.

(ϕ_1 liquid, ϕ_2 saturated vapour.)

HEPTANE.						
Temp.	θ	ϕ_1	ϕ_2	$\phi_1 - \theta \log_e \phi_1$	$\phi_2 - \theta \log_e \phi_2$	$\frac{3-\theta}{2}$
80	0.654	1.391	0.204	1.175	1.243	1.173
140	0.765	1.346	0.347	1.119	1.157	1.118
180	0.839	1.307	0.457	1.083	1.114	1.081
220	0.913	1.253	0.593	1.047	1.070	1.044
250	0.969	1.182	0.739	1.020	1.032	1.016
METHYL PROPIONATE.						
80	0.666	1.391	0.217	1.171	1.234	1.167
180	0.854	1.299	0.485	1.076	1.103	1.073
255	0.996	1.100	0.879	1.005	1.007	1.002

The "reduced" equation (11) is tested in Table IV., which shows the same imperfect agreement for vapours and good fit for liquids.

4. The relations obtained above give a means of calculating the critical temperature and critical density of substances for which these data have not been found by direct measurement.

For instance, equation (11) may be rewritten in the form

$$\frac{3}{2}\psi - \theta \log_e \frac{3}{2}\psi = \frac{3-\theta}{2}, \text{ if we write } \psi \text{ for } \frac{\rho^{1/3}}{\rho_1^{1/3}}.$$

This reduces, for calculation, to

$$T_c = \frac{0.0630 - 1.535 \log \psi}{1 - \psi} T.$$

It is found that for saturated vapours the quantity ρ_0 must be replaced by successively smaller values as one goes from higher to lower temperatures in order to force a fit with equation (4). At the lowest temperatures good agreement is found if one replaces ρ_0 by ρ_1 . Using this purely empirical fact, we have for vapours of low densities the relation

$$T_c = - \frac{2 \log_e \psi}{3(1-\psi)} T. \quad . \quad . \quad . \quad . \quad (14)$$

Thus, applying (13) to liquid mercury at 260°C. , $\psi = 0.960$, taking $\rho_1^{1/3}$ as 2.447 (Table II.). The calculated value of T_c is 1209°Abs. or 936°C. From the data for 360°C. we find 1032°C. for T_c .

Using (14) for mercury vapour at 180° , 220° , and 260°C. , we find respectively 998° , 981° , and 972°C. as the critical temperature.

Again we may evaluate this temperature from the relation $\alpha = \frac{\rho_c^{1/3}}{T_c} = \frac{2\rho_1^{1/3}}{3T_c}$. For mercury α is 1.28×10^{-3} , whence T_c is 996°C.

These estimates then agree in suggesting that the critical temperature of mercury is about 980°C. and its critical density about 4.35. Assuming the quantity $\frac{RT\rho}{p}$ at the critical temperature to be of its usual order of magnitude, the critical pressure indicated is about 600 atmospheres.

5. We may then conclude that the density of a fluid is represented by an expression of the form $\rho = \rho_0 e^{-\frac{V}{RT}}$, where the energy term $V = E_0 - B\rho^{1/3}$. E_0 is characteristic of each substance and is independent of the temperature and state of aggregation. The difference between V_1 , the value for the liquid form at any temperature T , and V_2 , the value for the saturated vapour at the same temperature, represents the difference between the amounts of work done when the molecules are dissipated beyond each others' range of attraction, according as we start with the liquid or the vapour phase. We should accordingly expect the work $V_2 - V_1$ to be intimately related to the internal latent heat of vaporization at the temperature T . Now $V_2 - V_1 = RT \log_e \rho/\sigma$, from (1), and it is well known that the internal latent heat of vaporization is represented with considerable accuracy by the expression $CRT \log_e \rho/\sigma$, where C is a number, approximately 1.7 to 2, varying somewhat for different substances, and rising slowly with temperature near the critical point to the latter figure, 2.

Further, Mills has shown that the internal latent heat is also given with some accuracy by an expression of the form $K(\rho^{1/3} - \sigma^{1/3})$, where K is constant for a given substance. Mills derived this expression on the assumption that the law of attraction between molecules is that of the inverse square. From considerations of surface tension and many other properties of liquids we know that such a law of force is impossible, and Mills's work has consequently been strongly criticised and has perhaps not received the attention it deserves. From equation (5) we see that if the internal latent heat is equal to $CRT \log_e \rho/\sigma$, it must also be given by Mills's expression. The latter results, in fact, not from any particular form of the law of intermolecular force, but from purely kinetic considerations, as set forth in the first section above.

6. The "maximum density" ρ_0 is given by equation (8) above in terms of the critical density. From ρ_0 we may calculate the diameter of a molecule of the substance. A few values are given in the first column of Table V.; the two other columns give the values drawn from measurements of viscosity, (a) by the usual equations, (b) as given by Sutherland. These data are quoted from Kaye and Laby's Tables.

A large number of molecular diameters have been calculated in this way and the data obtained will be discussed in a further paper.

TABLE V.
Molecular Diameters.

Substance.	From $\rho_0 = e^{3/2}\rho_c$.	From Viscosity Measurements.	
		(a)	(b) Sutherland.
Hydrogen	2.88	2.47	2.17
Helium	2.82	2.18	1.92
Argon.....	3.03	3.36	2.66
Nitrogen	3.21	3.50	2.95
Oxygen	3.01	3.39	2.71
Nitrous Oxide	3.30	4.27	3.33
Carbon Monoxide...	3.21	3.50	2.74
Carbon Dioxide ...	3.27	4.18	2.90

Summary.

It is shown that the density ρ of a fluid can be represented by the equation

$$\rho^{1/3} - \alpha T \log \rho^{1/3} = \rho_1^{1/3} - \alpha T \log \rho_0^{1/3},$$

where ρ_0 is the "maximum" density of the substance, and ρ_1 and α are constants. Further $\alpha = \rho_c^{1/3}/T_c$, where the subscript denotes data at the critical temperature.

It is shown that $\rho_1^{1/3} = \frac{3}{2}\rho_c^{1/3}$ and $\rho_0^{1/3} = e^{1/2}\rho_c^{1/3}$. A "reduced" equation containing no constants peculiar to a particular substance is also obtained. These equations hold very closely for liquids, approximately for saturated vapours.

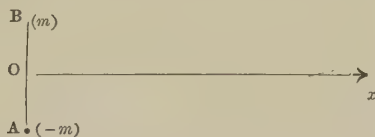
The internal latent heat of vaporization L_i is discussed and it is shown that Mills's Equation $L_i = K(\rho^{1/3} - \sigma^{1/3})$ (ρ = density of liquid, σ = that of vapour) can be deduced from kinetic considerations and does not depend as he supposed upon an inverse square law for intermolecular attractions.

From the "maximum" density ρ_0 the diameters of molecules can be estimated.

CVI. *On a Simple Light-Quantum.*
 By Prof. E. T. WHITTAKER, F.R.S.*

THE light-quantum described below is a solution of the ordinary Maxwell's equations of the electromagnetic field, and therefore behaves in accordance with the "classical" theory so far as refraction, interference, polarization, etc., are concerned. But it has the property, which is required for "quantum" phenomena, that if, after it has travelled any distance, however great, from its source, it encounters an atom, then the atom will in certain cases absorb *the whole* of the energy of the light-quantum, even though that energy was, immediately before the encounter, distributed over a very large region of space.

Consider first an ordinary elementary magnetic molecule at a point O, whose axis is in the line AB. We shall for the moment regard this in the old-fashioned way as the limit of



a positive magnetic charge m at the point B, together with a negative magnetic charge $-m$ at the point A. This molecule sets up a magnetic field extending over all space.

The ordinary law of action of magnetic charges asserts that the charges at A and B attract each other, so they must be supposed to be kept apart by some arrangement in the material molecule in which they are embedded.

Now, let Ox be a direction at right angles to AB, and suppose that the magnetic molecule is set in motion in the direction Ox . Since a moving magnet generates an electric field which can act on another moving magnet, the force between the charges A and B is now affected by this additional force, which diminishes the original force between them. As the velocity of the magnetic molecule along Ox increases, the total force between the two charges continually decreases, until in the limit when the molecule is moving with the velocity of light, the force is exactly null: the electromagnetic force due to the motion exactly neutralizes the purely magnetic force. Thus if the molecule is moving

* Communicated by the Author.

with the velocity of light, we have no longer any need of the material framework to keep the two charges apart, and we can suppose the charges completely disembodied.

Now consider what has happened to the field. As was shown long ago by Heaviside, when the molecule is set in motion in the direction Ox , the lines of magnetic force due to the molecule tend to draw in nearer to the molecule so far as the direction Ox is concerned, so that they concentrate towards the plane through O perpendicular to Ox ; until in the limit, when the velocity of the molecule is the velocity of light, the lines of force are entirely confined to this plane (which, of course, is travelling with the velocity of light), the field in the rest of space being null. There will now be lines of electric force (due to the motion of the magnetic charges) as well as lines of magnetic force, and the lines of electric force will be everywhere perpendicular to the lines of magnetic force: in short, what we now have is essentially a plane wave of ordinary light. The original magnetostatic field has become a plane wave of light, by merely setting it in motion with the velocity of light.

This plane wave of light, however, will have two peculiarities which distinguish it from the plane wave of light of the ordinary text-books. In the first place, the intensity of the disturbance is not the same over the whole of the infinite plane wave-front, but diminishes as we go outwards from the centre O of the plane, and is null at infinity. This is a satisfactory feature, since Baldwin and Jeffery have shown recently* that the old-fashioned plane-wave, with its intensity the same all over its infinite front, is an impossibility in general relativity. In the second place, our wave has a singularity at the point O , representing, in fact, the disembodied form of the magnetic molecules with which we started. This singularity we shall call the "*speck*" on the wave-front.

As a matter of fact, if we take the axis of z along AOB , and take an axis of y at right angles to the axes of x and z , then the electric force (E_x, E_y, E_z) and the magnetic force (H_x, H_y, H_z) in the wave-front are given by the equations

$$\begin{aligned} E_x &= 0, & E_y &= \frac{\partial}{\partial z} \left(\frac{z}{y^2 + z^2} \right), & E_z &= -\frac{\partial}{\partial y} \left(\frac{z}{y^2 + z^2} \right), \\ H_x &= 0, & H_y &= -E_z, & H_z &= E_y, \end{aligned}$$

and this field satisfies Maxwell's equations, except at the point ($y=0, z=0$), which is the "*speck*."

* Proc. Roy. Soc. cxi. p. 95 (1916).

It is the "speck" which confers on the wave the desired "quantum" properties, for in the original magnetostatic field, anyone who takes hold of the magnetic molecule and moves it about, thereby moves the whole of the magnetic field; the magnetic field is, so to speak, led captive by the magnetic molecule. This property—that the whole field is an appanage of the magnetic molecule and can be carried about with it—still persists in the limiting case which we have considered, in which the magnetic molecule has shed its materiality and has become the "speck" on the wave-front of the light: it is still true that anyone who can take hold of and capture the "speck" thereby captures the whole of the energy in the light-wave, which is really a mere appanage of the "speck."

Now the "speck" retains the property possessed by the original magnetic molecule, of being acted on by magnetic forces (and, since it is in motion, by electric forces also); and therefore, if the "speck" happens to impinge on an atom, or to pass very near to one, there is a possibility that the speck may be attracted into the atom and swallowed up and, so to speak, digested by it. The result will be that *the whole* of the energy in the light-wave will now have become the property of the atom: it may be partly located in the space outside the atom, but it belongs to the atom in the sense that wherever the atom moves, this bundle of energy henceforth moves with it. Thus the theorem which Einstein many years ago deduced from thermodynamic reasoning, namely, that *every parcel of light-energy which is emitted from an atom is ultimately entirely absorbed by a single other atom* is here seen to be a consequence of the strict classical electromagnetic theory of light. If this fact has not been clearly perceived before, it is because the expounders of the classical theory have been led astray by that artificial and (as we now know) physically impossible creation of mathematical analysis, the infinite plane-wave of light.

October 4th, 1926.

CVII. *On the Rate and Mechanism of the Aeration of Water under Open-Air Conditions.* By W. E. ADENEY, D.Sc., F.R.C.Sc.I., F.I.C.*

THE problems of the rate at which the solution of oxygen and nitrogen occurs at the exposed surfaces of waters under open-air conditions, and of the mechanism by which the dissolved gases are transmitted to the unexposed portions of such waters, have become of considerable technical importance, especially in connexion with the disposal of normal sewage liquors by dilution with clean river waters, as recommended by the Royal Commission on Sewage Disposal in its eighth Report (1912), and also in connexion with the economical operation of the Bio-Aeration method of sewage purification.

A large number of experiments have been made in connexion with these problems—first by the writer (1), then by him in collaboration with the late Mr. H. G. Becker (2), and latterly by him in collaboration with Dr. A. G. G. Leonard and Miss A. Richardson (3).

Solution of Gases by Well-Mixed Water in Thin Films.

Adeney and Becker employed a method for determining the rates of solution of oxygen and nitrogen from the air by water, every part of which is successively exposed in thin films, and becomes aerated independently of downward "streaming."

The method consists of enclosing a large bubble of air of known volume in a long narrow tube containing de-aerated water, also of known volume, and of allowing the bubble to ascend through the water column repeatedly until saturation of the water by air has been reached, the water-air surface remaining unbroken throughout the experiment.

The time taken by the bubble to ascend the tube was measured in every case, and found to be practically constant, at 18 seconds per double journey.

The loss of pressure in the bubble of air was measured, after each double passage up the tube, by means of a water manometer, and afforded the necessary data for calculating the amount of gas dissolved, step by step, until saturation was reached.

The air in the bubble was renewed after each observation,

* From the Scientific Proceedings of the Royal Dublin Society for April 1926. Communicated by the Author.

by taking out the stopper of the tube and inserting into the air-space a tube connected with a filter-pump, which drew a current of air through the space.

As the bubble of air ascends the tube from the bottom, the whole of the water gradually and uniformly flows over it in thin films, the mass of the water forming the films becoming mechanically and intimately mixed, after exposure of their surfaces to the air in the bubble, with the result that the column of water, when the experiment is properly carried out, becomes gradually charged with small additions of air throughout its length, by repeated passages of the bubble along the tube, until saturation is reached. So that the air-content of the column of water is uniform throughout its length at any intermediate stage of solution up to saturation. Bubbles of air of 5, 7.5, 10, 12.5, and 15 c.c. in volume were employed.

In the case of the bubble of 15 c.c. in volume, the thickness of the film was found to be 0.05 cm., and its effective area 71.33 sq. cm.

The solution of oxygen and nitrogen was found to take place in accordance with the formula

$$w = w_1 - (w_1 - w_0) e^{-f \frac{a}{v} t}$$

in which w = concentration at the end of t seconds.

w_1 = saturation concentration at the given temperature and pressure.

w_0 = initial concentration at start, when $t=0$.

f = coefficient of escape of the gas from the water per unit area.

v = volume of water.

a = area of surface exposed.

The coefficient f varies with temperature according to the equations

Oxygen $f = 0.0096 (T-237)$ per second.

Nitrogen $f = 0.0103 (T-240)$ „ „

Air $f = 0.0099 (T-239)$ „ „

It is noteworthy that, when the rates of solution are expressed in percentages of saturation, the curves drawn from the percentages of saturation for the three gases lie very close to each other, those for oxygen and nitrogen (pure) being practically identical.

It is possible to calculate, with the aid of this formula, the rate of solution of oxygen or nitrogen from the air, by films of fresh or salt waters, under different conditions of area of film and total volume of water, or initial degree of saturation, provided that the calculations are based upon data derived from experiments carried out so that all of the water is successively exposed in thin films, and thorough mixing is thus ensured.

From the results of the experiments described in the papers, Nos. 31 and 44 (2), and with the aid of the above formula, the rate of solution of oxygen from the air by films of fresh and of sea water, 0.05 cm. thick, have been calculated for temperatures between 0° C. and 30° C. The values obtained are given in Table I.

TABLE I.

Rates of Solution of Oxygen, expressed in Percentages of Saturation, by Films of De-aerated, Fresh, or Salt, Waters, 0.05 cm. thick, when uniformly exposed to the Air, and independent of Evaporation and downward "Streaming."

Temperature	0°	5°	10°	15°	20°	25°	30° C.
Percentage of saturation	Time in seconds.						
10	... 1.0	0.8	0.8	0.7	0.7	0.6	0.5
20	... 2.1	1.8	1.6	1.4	1.3	1.3	1.2
30	... 3.2	2.7	2.3	2.0	1.8	1.7	1.6
40	... 4.5	4.0	3.6	3.3	2.9	2.7	2.4
50	... 6.0	5.2	4.6	4.2	3.9	3.6	3.3
60	... 8.0	7.2	6.4	5.7	5.0	4.6	4.3
70	... 10.5	9.3	8.2	7.3	6.7	6.1	5.8
80	... 14.0	12.5	11.0	10.0	9.0	8.3	7.7
90	... 19.8	17.5	15.6	14.2	13.0	11.9	10.8
99	... 39.6	35.0	31.2	28.4	26.0	23.8	21.6

Pressure, 760 mm. (moist).

For practical purposes these values may be taken as approximately representing the maximum rates of solution of oxygen from the air by the exposed surfaces of water exposed to open-air conditions, at the given temperatures, independently of evaporation and downward "streaming."

Solution of Gases by Quiescent Columns of Water.

In the case of quiescent columns of de-aerated water, freely exposed to the air, the dissolved atmospheric gases do not remain concentrated at the surface film. The latter, on the contrary, as the gases are dissolved by it, sinks towards the bottom of the column, for the reasons given below, with the result that the column becomes aerated gradually, and more or less uniformly, from top to bottom during every step of the process of aeration, until completely aerated. At no time does the surface layer of a column of de-aerated water become saturated until the whole column of water throughout its depth is also nearly saturated.

From the results of the writer's experiments with three- and six-foot columns of water, and from those of the experiments recently carried out with great care in collaboration with Dr. A. G. G. Leonard and Miss Richardson with ten-foot columns of distilled water and of solutions of sodium chloride of various concentrations, it has been established that the aeration of quiescent columns of de-aerated water, both fresh and salt, under open-air conditions, is to be ascribed largely, though possibly not wholly, to the effects of evaporation from the exposed surfaces of the water.

Apparently, as evaporation proceeds from the surface of a body of quiescent water, the density of the exposed surface film of water is increased relatively to that of the unexposed portions of the water as a result of cooling, and also, in the case of salt waters, of concentration of the salts in solution, and the denser water sinks in minute imperceptible streamlets towards the bottom. The continuous downward "streaming" thus produced causes a corresponding upward displacement of unexposed portions of the water, and sets up an imperceptible, but efficient, process of mechanical mixing of the aerated surface film with the unexposed portions of the water. Although the mass of the water "streaming" downward from the exposed surface at any particular time must be relatively minute, it passes vertically downwards through the mass of water below the surface towards the bottom, and sets up a very efficient process of mixing, especially in the case of salt water. And since the experiments referred to above prove that the downward "streaming" is effective in causing as uniform mechanical mixing to depths of 10 feet as to 1, 3, and 5 feet, it may

safely be assumed that it is effective in producing a similarly uniform mixing down to much greater depths.

The "streaming" sets up a more rapid and uniform process of mixing in salt waters than in fresh waters when the conditions obtaining over their exposed surfaces are favourable for free evaporation, owing, no doubt, largely, if not wholly, to the fact that in addition to the cooling effect of evaporation at the exposed surface film, there is also that of concentration of the salts in solution in the case of the former class of waters.

It may be noted, furthermore, that the process of "streaming" also proceeds more rapidly and uniformly at temperatures at and above 10°C . than below it in both fresh and salt waters. This is to be expected from the slow rate of evaporation at the lower temperatures, and from the fact of fresh water attaining its maximum density at 4°C .

It also depends upon the concentration of the salts in solution. The optimum concentration is equivalent to about 1.5 per cent. sodium chloride.

It may finally be concluded that there are five conditions upon which the mechanism of the aeration of fresh and salt waters, under open-air conditions, primarily depends. They are :—

- (1) The area of water exposed to the air ;
- (2) temperature ;
- (3) humidity of the air ;
- (4) salinity (in the case of tidal waters) ;
- (5) wind, causing both an increase in area exposed and an acceleration of evaporation per unit area.

The influence of the humidity of the air and of the salinity of the water upon the rate of "streaming," and therefore upon the rate of mixing of the exposed with the unexposed portions of a water, has recently been quite independently confirmed by Dr. J. A. N. Friend's interesting and important experiments on the corrosion of iron (4).

The area of open waters exposed, in common with the other conditions, will not remain constant, but will be liable to considerable variation, according to the force of the wind or of water currents, or of both.

The turbulent action of these two factors will also effect a more or less rapid increase in the rate of solution of atmospheric gases by the exposed surface films of the water.

The formula applicable to the calculation of the rate of aeration of wholly or partly de-aerated quiescent columns of fresh and of sea waters, when their exposed surfaces are undisturbed, and the humidity and temperature of the air are uniform, is of the same form as that above given for the rate of solution of oxygen and nitrogen by thin films of water, when independent of evaporation and downward "streaming" (2, xvi. 13).

The effect of the humidity of the air in contact with the water on the rate of aeration is shown by the following experiment:—

Four tubes, each 320 mm. long and 40 mm. diameter, were placed in a thermostat after being filled with de-aerated water. The upper ends of three of these tubes, after 50 c.c. water had been withdrawn from each, were connected in series by means of rubber corks and glass tubing, so that a current of air could be drawn through the air-spaces. The fourth tube was left open to the atmosphere.

Unfiltered air was drawn through the air-space of tube 1, then through two U-tubes containing calcium chloride, and thence into the air-space of tube 2, whence it passed directly into the air-space of tube 3. Thus the air was much drier when passing through the air-space of tube 2 than when passing through the air-space of tube 1; while the air on being drawn through the air-space in tube 3 was nearly, if not wholly, saturated with aqueous vapour.

Tube 4 was exposed to the open air in the middle of the thermostat, where the humidity of the air was considerable.

The results obtained from this experiment are given in Table II.

TABLE II.

Experiment showing the Effect of the Humidity of the Air on the Rate of Aeration of Quiescent Columns of Distilled Water. Temperature, 15° C.

No. of tube.	Depth of water.	Degree of aeration in p.c. of saturation*.	Value of f_1 .	Time of Exposure.	
				Actual.	Calculated from rate of solution at surface at 15° C. (Table I.)
	cms.		per hour.	hours.	minutes.
1	27·07	41·5	0·34	43·0	22·8
2	26·37	63·2	0·61	44·0	46·9
3	26·69	31·3	0·23	44·5	10·9
4	30·20	32·7	0·29	42·0	13·6

* Initial aeration of each column = 10·3 per cent. saturation.

Area of surface of column 1 = 12.56 sq. cm., of each of the other columns = 12.25 sq. cm.

f_1 = coefficient of escape per unit area.

On examining these results it will be noticed that the column exposed to the dried air absorbed more than twice as much air as the column exposed to the moist air.

It may be noted, in connexion with the above experiment, that the values of f_1 in other experiments with quiescent columns of fresh, and of sea waters, when exposed to fresh air and kept at as uniform a temperature as possible, were found to be equal to 0.388 and 0.509 respectively.

The figures in the last column of the above table give the times in which the columns would have been aerated to the percentages of saturation which they respectively attained under the conditions of the experiment, had the aeration of each column proceeded at the rate given in Table I. for surface films .05 cm. thick, at 15°C.; that is, at the approximately maximum rate of solution of oxygen from the air by fresh and salt waters, as found by the bubble method for the same temperature.

On comparing these figures with the actual times of exposure given in the table, it appears that the rates of aeration of quiescent columns of water by "streaming," under the specified conditions, were about 113, 56, 245, and 185 times slower than the initial rate of solution by the surface film, .05 cm. thick, according to the humidity of the air passing over their exposed surfaces.

These rates of aeration apply only in cases of experiments with water columns in the laboratory, in which the surface layers can be preserved undisturbed without difficulty.

Under natural conditions, however, the exposed surface of open water is usually in a more or less disturbed condition, and then the aeration by "streaming" becomes greatly accelerated, as shown by the following experiment, in which the exposed surfaces of quiescent columns of de-aerated fresh and sea waters were kept in a continuous state of gentle disturbance. In this experiment two tubes, each 110 cm. long and 5 cm. diameter, were nearly filled, one with de-aerated fresh water, and the other with de-aerated sea water. A fine glass rod stirrer, bent into the shape of a gridiron, 4 cm. broad, was fixed so that its lower end dipped 2.5 cm. below the surface of the water in each tube, and was mechanically rotated slowly for 19 hours, the speed being such that the surface was only moderately ruffled. At the end of this time the stirrers were stopped, and samples were drawn from the top and bottom layers of

the water column in each tube, and the dissolved nitrogen content was determined with the following results :—

TABLE 3.

	Sea water.		Fresh water.		
	Top layer.	Bottom layer.	Top layer.	Bottom layer.	
At commencement ...	10·7	10·7	9·2	9·2	per cent. saturation.
19 hours later ...	98·3	96·5	80·4	73·4	per cent. saturation.

Temperature of each column, 8·3° C.

It is evident from the above results that, when the surface of the water is kept continuously and gently disturbed, the effective area exposed to the air becomes so much increased that the downward “streaming” is greatly augmented, with a corresponding acceleration of the rate of aeration of the whole column. And this is true when the experiment is carried out at the low temperature of 8·3° C. The results recorded in the table show that in the course of 19 hours the average aeration of the sea- and fresh-water columns was increased, on an average, from 10·7 and 9·2 to 97·4 and 76·9 per cent. saturation respectively.

These columns would have reached like degrees of partial aeration in approximately 13 and 5·5 hours respectively had their exposed surfaces remained undisturbed, and had the aeration of the columns proceeded at the initial rates of solution of oxygen as found by the bubble experiments.

It may, therefore, be fairly assumed that the minimum rates of aeration of open waters by “streaming” may be approximately twofold and fourfold slower respectively than the rate that would be found by calculation for the given depth from the results of the bubble experiments.

These rates of aeration for open waters may fairly be regarded as minimum rates, since the temperature at which the experiment was carried out was below 10° C., and since the air immediately above the columns of water must have been well charged with aqueous vapour during the experiment, owing to the fact that their surfaces were exposed to air partially enclosed within the mouths of the tubes containing the water.

In the Bio-aeration method of purification the sewage liquid is intimately mixed, while in the aeration tank, by blowing air through it from the bottom of the tank, or by a propeller partially submerged in it. Whichever means of mixing is adopted, the surface of the sewage liquid is kept

in a state of turbulent agitation, and it will probably be found on investigation that the minimum rate of aeration of the sewage liquid by downward "streaming" will be fully equal to, or, owing to the greatly increased surface area, may even exceed, that found by calculation from the results obtained by the bubble experiments for the given depth of the liquid, assuming an effective absorbing area equal to the undisturbed surface area of the tank.

The author desires to express his indebtedness to Dr. H. H. Poole, Editor of the Scientific Proceedings of the Royal Dublin Society, for valuable suggestions given in the preparation of this communication for publication.

References.

- (1) Adeney.—"Unrecognized Factors in the Transmission of Gases through Water." *Sci. Trans. Roy. Dub. Soc.* 1905, viii. 13, p. 161; also *Phil. Mag.* 1905, ix. p. 630. See also supplementary volume vi. to the 5th Report of the Royal Commission on Sewage Disposal, 1908, Cd. 4284, p. 56.
- (2) Adeney and Becker.—"On the Determination of the Rate of Solution of Atmospheric Nitrogen and Oxygen by Water." *Sci. Proc. Roy. Dub. Soc.* 1918, xv. 31, p. 385; 1919, xv. 44, p. 609; 1920, xvi. 13, p. 143; also *Phil. Mag.* 1919, xxxviii. p. 317; 1920, xxxix. p. 385, and 1921, xlii. p. 87.
- (3) Adeney, Leonard, and Richardson.—"On the Aeration of Quiescent Columns of Distilled Water and of Solutions of Sodium Chloride." *Sci. Proc. Roy. Dub. Soc.* 1922, xvii. 3, p. 19; also *Phil. Mag.* 1923, xlv. p. 837.
- (4) Friend.—"The Corrosion of Iron in Water and in Neutral Salt Solutions." *J. C. S.* 1923, cxxiii. p. 2996.

CVIII. *On an Apparent Relation between the Rate in the Change of the Electric Resistance at Fusion and the Crystal Lattice of Metallic Elements.* By HARALD PERLITZ, Assistant Professor of Theoretical Physics, University of Tartu*.

1. **T**HE electric resistance of metallic elements changes abruptly at fusion in such a way that the phase with the smaller specific volume has the smaller resistance†. The structure of metallic elements also suffers a sudden change at fusion, and as melting means a complete collapse

* Read at a meeting of the Naturalists' Society at Tartu, March 18, 1926. Communicated by the Author.

† P. W. Bridgman, *Phys. Rev.* (2) xvii. p. 61 (1921).

of the systematically arranged crystal lattices formed by the atoms of metallic elements in the solid state, in the place of which there appears a chaotic distribution in the liquid state, it is natural to look for a relation between the discontinuity of the electric resistance at fusion and the crystalline lattice of metallic elements. For this purpose the following table was compiled:—

TABLE.

Element.	Type of lattice ¹ .	Rate of change in resistance at fusion ² .	Mean rate.	Group-value.
Bismuth	Rhombohedral hexagonal.	·465 ⁵ ; ·467(5) ⁶ ; ·476(5) ⁶ ; ·47; 1/2 ⁶ ; ·43; ·45; ·45	·48	1/2
Gallium	Not determined.	·48 ⁵ ; ·58	·53	
Antimony.....	Rhombohedral hexagonal.	·70; 67 ⁷	·69	
Sodium.....	Body-centred cubic.	1·37 ⁵ ; 1·34; 1·6 ⁸ ; 1·45; 1·44; 1·53 ⁹	1·45	3/2
Lithium	Body-centred cubic.	2·51 ¹⁰ ; 1·68; 1·27 ⁹	1·48 ¹²	
Potassium ...	Body-centred cubic.	1·44 ⁵ ; 1·39; 1·5 ⁹ ; 1·56; 1·53; 1·60 ⁹	1·50	
Rubidium.....	Not determined.	1·81 ¹¹ ; 1·58 ⁵ ; 1·5 ⁸	1·54 ¹³	
Aluminium ...	Face-centred cubic.	1·65	1·65	
Cæsium	Not determined.	1·7 ⁵ ; 1·65; 1·7 ⁸ ; 1·79 ⁹	1·71	2
Silver	Face-centred cubic.	1·98; 1·74	1·86	
Cadmium.....	Hexagonal close-packed.	1·8 ⁵ ; 1·96 ⁵ ; 1·97	1·91	
Lead.....	Face-centred cubic.	1·9 ⁵ ; 1·95 ⁵ ; 2·06	1·97	
Thallium	Uncertain ³	2·0 ⁵	2·0	
Copper	Face-centred cubic.	2·09; 1·97	2·03	
Zinc	Hexagonal close-packed.	2·0; 2·09	2·05	
Tellurium.....	Rhombohedral ⁴ .	2·1 ⁵	2·1	4(?)
Tin (rhombic).	Not determined.	2·10; 2·2 ⁵ 2·21 ⁵ ; 2·12; 2·02	2·13	
Gold	Face-centred cubic.	2·28	2·28	
Mercury	Tetrahedral hexagonal.	4·1; 4·09; 4·05; 4·90; 5; 3·21	4·23	

¹ Authority, if not stated otherwise, Landolt-Börnstein, *Phys. chem. Tabellen*, pp. 865-867 (1923).

² Authority, if not stated otherwise, Landolt-Börnstein, *Phys. chem. Tabellen*, pp. 1051-1052 (1923).

³ Karl Becker & Fritz Ebert, *ZS. f. Physik*, xvi. p. 169 (1923); *Phys. Ber.* vi. p. 21 (1925).

⁴ A. J. Bradley, *Phil. Mag.* (6) xlviii. p. 490 (1924).

⁵ Ernst Wagner, *Ann. Physik* (4) xxxiii. p. 1486 (1910).

⁶ A. Guntz & W. Proniewski, *J. d. Chem. phys.* vii. p. 481 (1909).

2. Referring to the table, it should be mentioned that the change of resistance has hitherto been measured for 19 metallic elements, *i. e.* for roughly one-third of all metallic elements ; for 16 of them the crystal lattices have been determined. These data, gathered from the literature on the subject, have been collected in the above table, where the elements are arranged according to their average change of resistance. The crystal lattices given in the 2nd column are data obtained from X ray analysis

3. The 3rd column contains all available data for the rate of change of resistance at fusion, which in each horizontal line are arranged in chronological order. From these have been computed the average values given in the 4th column. In computing the averages all data in the 3rd column were taken into account, except in two cases, as stated in footnotes 10 and 11 ; questionable is the average for mercury, because the data for it exhibit too much variation.

4. If the supposition is correct that there exists a definite relation between the rate of change of the electric resistance at fusion and the crystal lattice, we should look for a relation between the data of the 2nd and 4th columns of the table. In this case we must first of all show that the average values in the 4th column are not distributed uniformly in the interval from the smallest to the greatest average, *i. e.* from .48 to 4.23, but that they cluster about certain values. This is

⁷ *Phys. Ber.* ii. p. 1048 (1921).

L. Hackspill, *Thèse*, p. 80 (Paris, 1912).

⁹ Deduced by myself from curves obtained by Charles C. Bidwell, *Phys. Rev.* (2) xxiii. p. 357 (1924).—For computing purposes the linear part of the curve for relative resistance, the part corresponding to the “ α form,” was prolonged to intersection with the melting-point ordinate ; the point of intersection was assumed as the relative resistance of the “ α form” at melting-point ; for this point was calculated the ratio of the relative resistance of the liquid phase to the relative resistance of the “ α form,” and the values obtained were used in compiling the table. For my purpose only figures 3, 6, 7, and 8, those for caesium, potassium, sodium, and lithium, could be used ; whilst figures 4 and 5, both for rubidium, were unsuitable (*l. c.* p. 366).

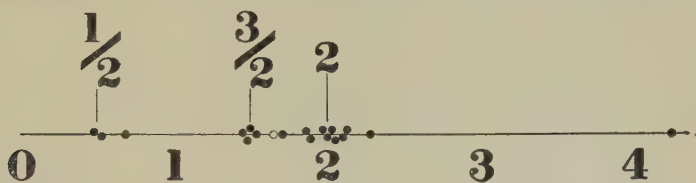
¹⁰ Arciero Bernini, *Phys. ZS.* vi. p. 78 (1905). The value 1.91, as stated in Landolt-Börnstein, *Phys. chem. Tabellen*, p. 1052 (1923), is due to misprints in A. Bernini's Table XIII.—As the conditions of A. Bernini's experiment do not warrant the purity of the metal, his data have not been used in computing the average.

¹¹ This value, computed by myself from Louis Hackspill, *Thèse*, p. 51, fig. 4 (Paris, 1907), has not been used, in computing the average, because L. Hackspill himself retracts it in his later investigation, *Thèse*, p. 71 (Paris, 1912).

¹² Compare the remark to footnote 10.

¹³ Compare the remark to footnote 11.

done best by constructing a distribution graph for these data as has been done on the figure, where all averages have been marked by black dots except that for aluminium, which is represented by a circle for the reason stated in paragraph 8.



5. The figure indeed displays a tendency for the average values alluded to to cluster round certain values which will be referred to as group-values. As such, disregarding the isolated value of mercury, the values $1/2$, $3/2$, and 2 may be taken.

6. Now, if our assumption holds good, there ought to be a relation between the group-values and the types of crystal lattices; in other words, metallic elements exhibiting common group-values should have lattices of the same type. On examining the data of the table for that purpose we find:—

7. The group-value $1/2$ is common to 3 elements: bismuth, gallium, and antimony. The lattices of bismuth and antimony are of the same type, whereas that of gallium has not yet been determined. Therefore: out of 3 cases, two are in favour of the assumption made, whereas regarding one it remains questionable.

8. The group-value $3/2$ is common to 6 elements: lithium, sodium, potassium, rubidium, caesium, and aluminium. Of these, sodium and potassium have body-centred cubic lattices, lithium has probably the same lattice* while the lattices of rubidium and caesium have not yet been determined. But considering that the elements of the second sub-group of the first groups, viz., copper, silver, and gold, have a lattice of the same type, it seems reasonable to suppose the same for the sub-group of the alkalis, *i. e.*, to assume a body-centred lattice for rubidium and caesium. As further evidence in favour of this assumption may be mentioned the relationship between atomic numbers and properties of ions†. If, however, we turn to the lattice of aluminium, we find it to be at variance with the former:

* A. W. Hull, *Phys. Rev.* (2) x. p. 691 (1917).

† Arthur F. Scott, *Journ. Ph. Chemistry*, xxix. p. 306 (1925).

it is of the face-centred cubic type. Therefore: out of 6 elements, three are in favour of the assumption made, whereas regarding two it remains questionable, and one, namely aluminium, is not in accordance with it: for this reason the position of aluminium in the figure has been indicated by a mark different from those for other elements.

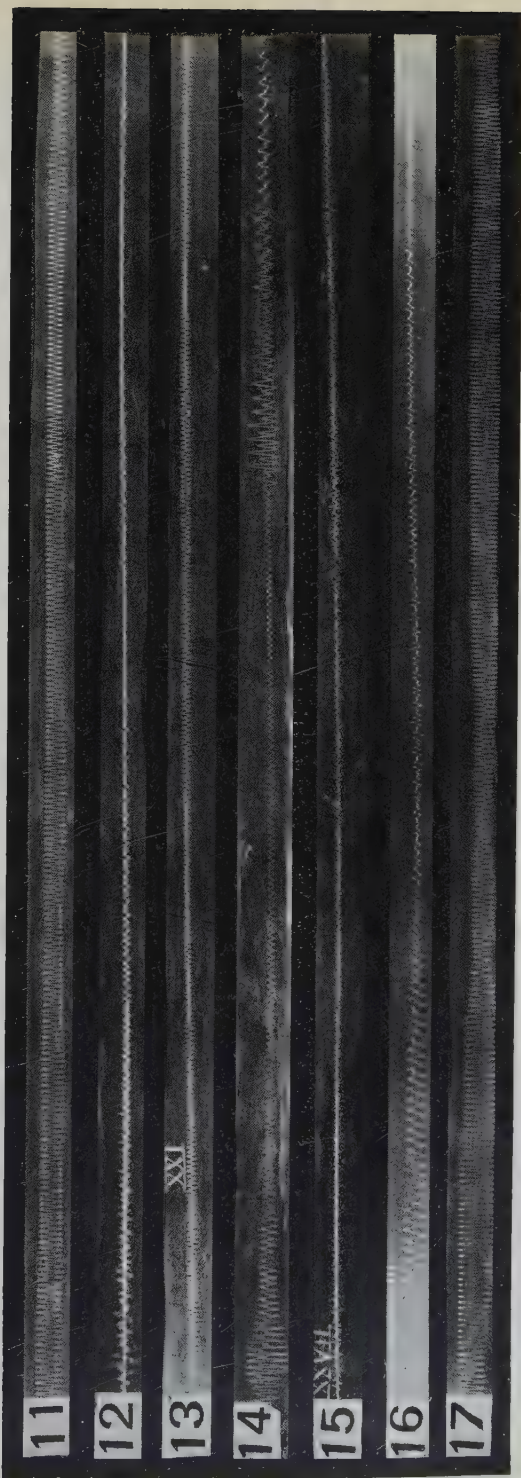
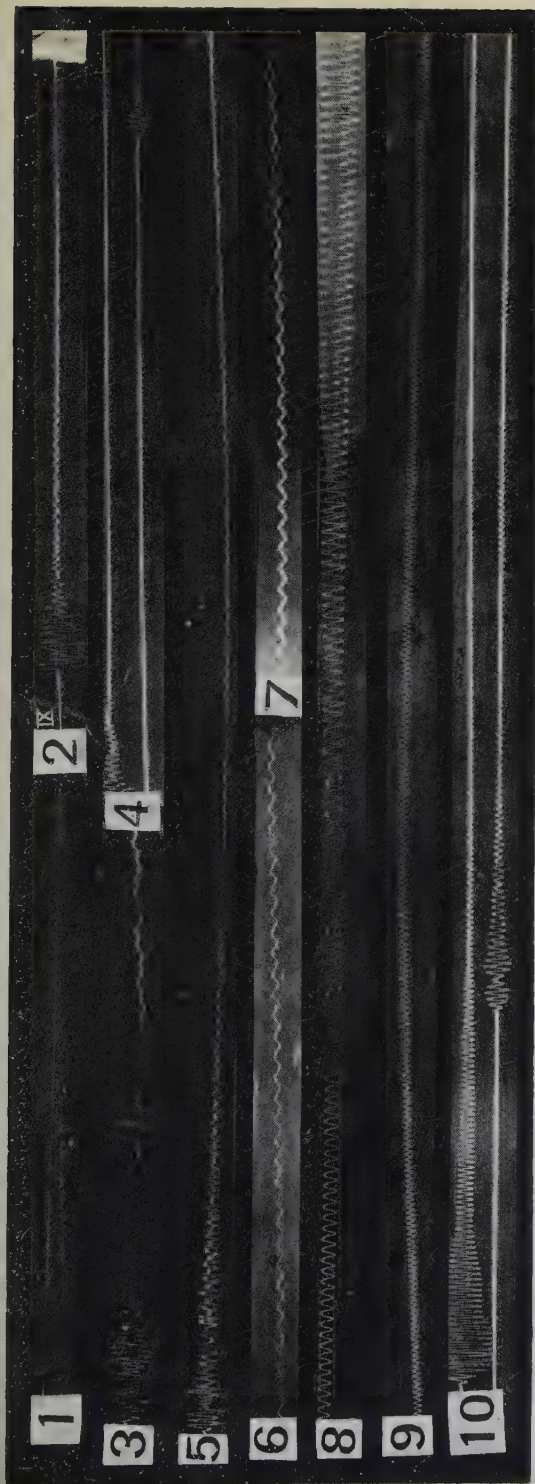
9. The group-value 2 is common to 9 elements: copper, silver, gold, lead, cadmium, zinc, thallium, tin, and tellurium. Of these, copper, silver, gold, and lead have face-centred cubic lattices, whilst cadmium and zinc have hexagonal lattices. But as the face-centred cubic and the hexagonal lattices referred to belong to the close-packed structure, the elements copper, silver, gold, cadmium, lead, and zinc may be united in one class—the class of the close-packed lattice. The lattice of the rhombic modification of tin, the modification which precedes the liquid phase, is still undetermined; so is the lattice of tellurium in the temperature interval immediately preceding fusion, and there is evidence for assigning to this lattice a form different from the lattice at indoor temperature*. Therefore: of 9 elements, six are in favour of the assumption made, whereas regarding three it remains questionable.

10. The group-value 4 (?) is shown only by mercury. As its lattice differs from the lattices of all other elements alluded to, this may be taken as an indirect evidence in favour of the assumption made.

11. Summarizing: Out of 19 elements, 12 elements are in favour of the statement that the rates of change of electric resistance at fusion are related to the crystal lattices of metallic elements, whereas regarding 6 elements the relation is still questionable, and divergence is exhibited by one element. The relation itself may be formulated into the following rough and ready rules:—

- (1) Metallic elements, the resistances of which at fusion change in the proportion of 1 : 2, have rhombohedral hexagonal lattices of the antimony type.
- (2) Metallic elements, the resistances of which at fusion change in the proportion of 3 : 2, have cubic body-centred lattices.
- (3) Metallic elements, the resistances of which at fusion change in the proportion of 2 : 1, have lattices of the close-packed type.

* A. Guntz & W. Broniewski, *J. d. Chem. Phys.* vii. p. 485 (1909).



18

19

20

21

22

23

24

25

FIG. 2.

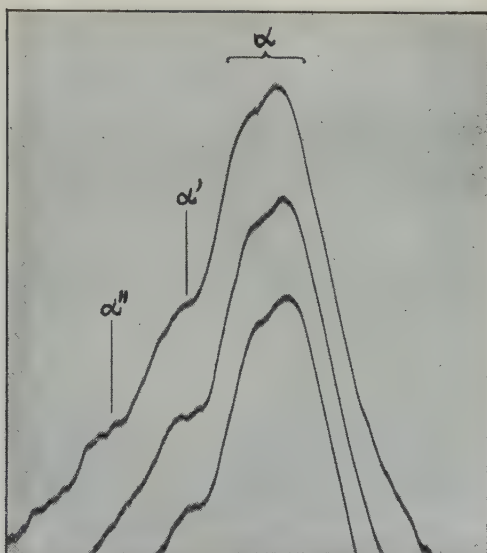


FIG. 5.

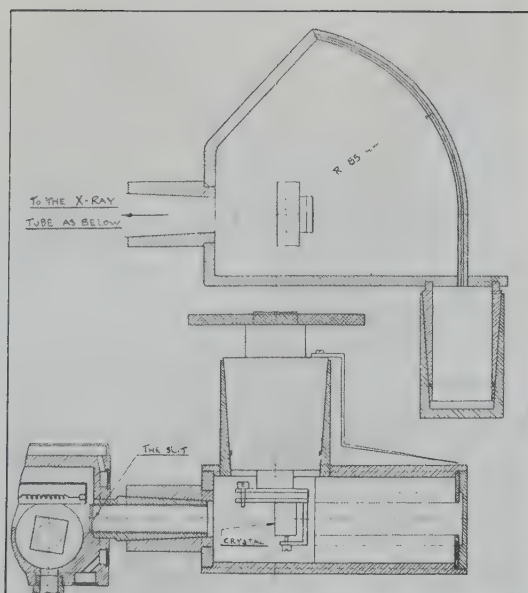
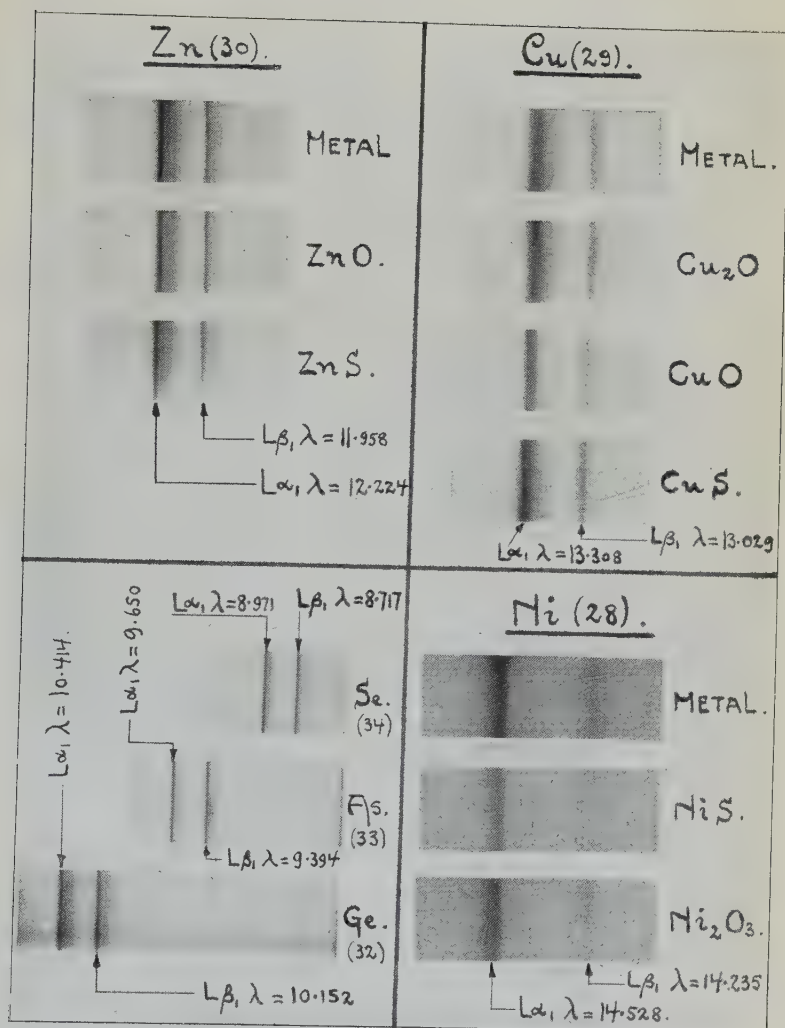
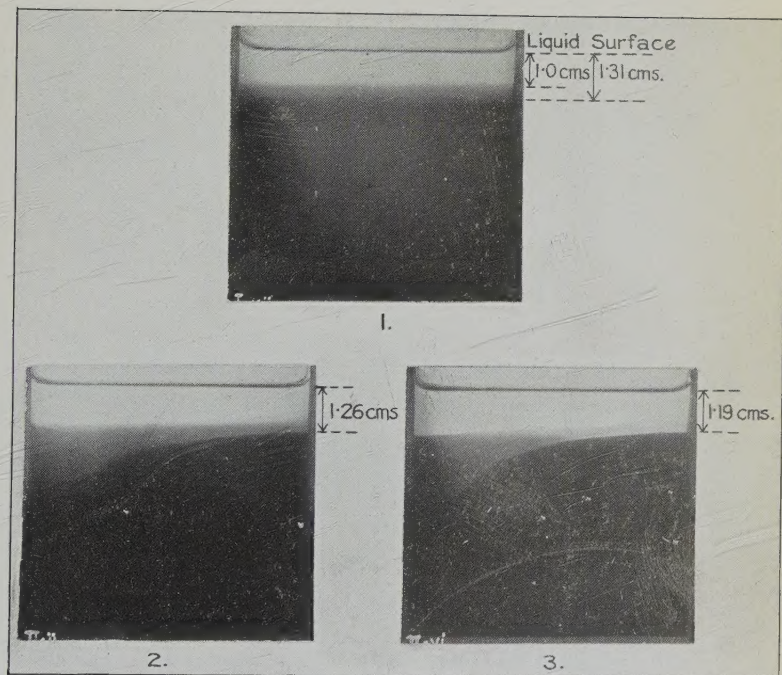


FIG. 3.

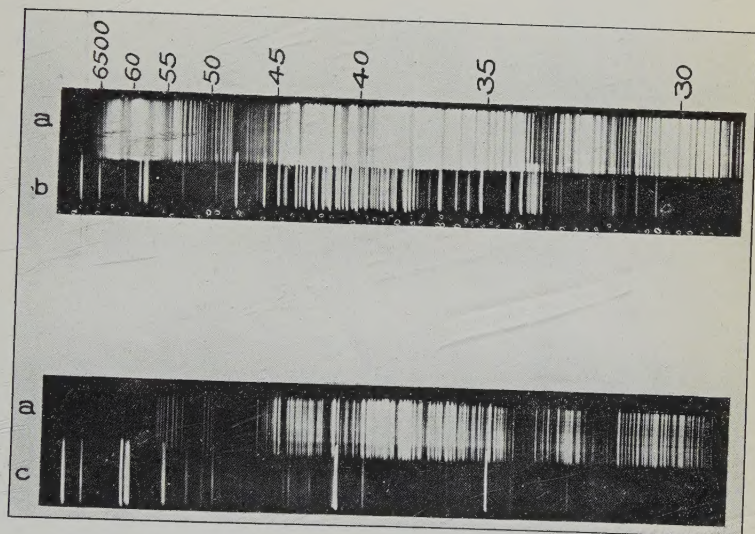


All the photographs are taken with a Gypsum Crystal,



COLLOIDAL SOLUTIONS OF COPPER.

1. After settling in dark for 18 hours (fig. 2, i.).
2. Light on right-hand side for 1 hour (fig. 2, iii.).
3. Light on right-hand side for $3\frac{1}{2}$ hours (fig. 2, vi.).



a. IRON COMPARISON SPECTRUM.

b. ENHANCED LINES OF POTASSIUM.

c. POTASSIUM ARC SPECTRUM.

